ENGINEERING POLYMERS BASED ON 1,1-DIPHENYLETHYLENE DERIVATIVES: POLYMER SUBSTRATES AS PRECURSORS FOR MEMBRANE DEVELOPMENT

by

MIZOLO GINETTE KASIAMA

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SUPERVISOR: PROFESSOR G J SUMMERS

Student number: 4122-623-2

I declare that the dissertation entitled: ENGINEERING POLYMERS BASED ON 1,1-DIPHENYLETHYLENE DERIVATIVES: POLYMER SUBSTRATES AS PRECURSORS FOR MEMBRANE DEVELOPMENT is my own work and that all sources that I have used or quoted have been indicated and acknowledged by means of complete references.

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(Ms M G KASIAMA)

ABSTRACT

A series of new, well-defined poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives containing the diphenylethylene moiety were prepared by step-growth polymerization methods.

Poly(ether ether sulfone) derivatives were prepared by two step-growth polymerization methods:

- (a) The cesium fluoride catalyzed polycondensation reactions of 4,4⁻-difluorodiphenylsulfone with different mole percentage ratios of silylated bisphenol derivatives, 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane and 1,1-bis(4-*t*-butyldimethylsiloxyphenyl)ethylene in N-methyl-2-pyrrolidone at 150 °C.
- (b) The potassium carbonate catalyzed nucleophilic aromatic substitution polycondensation reactions of 4,4´-difluorodiphenylsulfone with different mole percentage ratios of bisphenol A and 1,1-bis(4-hydroxyphenyl)ethylene in N,N-dimethylacetamide and toluene at 165 °C.

Poly(ether ether ketone) derivatives were prepared by the cesium fluoride catalyzed polymerization reactions of 4,4´-difluorobenzophenone with different mole percentage ratios of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane and 1,1-bis[4-(*t*-butyldimethylsiloxy)-phenyl]ethylene in N-methyl-2-pyrrolidone at 150 °C.

Polyimide derivatives were prepared by step-growth polymerization methods by the polycondensation reactions of 4,4'-oxydiphthalic anhydride with different mole percentage ratios of 2,2-bis[4-(4-aminophenoxy)phenyl]propane and 1,1-bis(4-aminophenyl)ethylene. The intermediate polyamic acids were subjected to thermal imidization processes to provide the corresponding polyimide derivatives.

Due to the regiospecific introduction of the 1,1-diphenylethylene group along the polymer backbone, the different poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives were subjected to post-polymerization sulfonation reactions via the thiol-ene reaction using sodium 3-mercapto-1-propane sulfonate as sulfonating agent and AIBN as initiator in N-methyl-2-pyrrolidone/dimethylsulfoxide at 75 °C for 5 days. The 1,1diphenylethylene derivatives and the different polymeric compounds were characterized by size exclusion chromatography, dilute solution viscometry, ¹H NMR and ¹³C NMR spectrometry, FTIR spectroscopy, thermogravimetric analysis, differential scanning calorimetry, X-ray diffraction, atomic force microscopy, transmission electron microscopy, elemental analysis, energy dispersive spectroscopy and ion exchange capacity measurements.

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DEDICATED TO MY PARENTS

Joachim Gisiati Kasiama and Viviane Milulu Mawaku

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CHAPTER 1

INTRODUCTION

Research emphasis on the development of renewable and clean energy strategies has recently received considerable interest in academia and industry. In particular, fuel cell technology has been considered as the alternative to fossil fuels for power generation because of its high electrical efficiency, low emissions and the use of materials which cause no environmental damage.^{1, 2, 3} Thus, polymer electrolyte membrane fuel cells (PEMFCs) have been developed as a promising alternative for vehicular transportation and for stationary and portable communications systems.

The electrolyte employed in PEMFCs is a solid polymeric membrane fitted between two platinum porous electrodes.⁴ Commercially available sulfonated based perfluorinated polymers, such as Nafion[®], Flemion[®], Dow[®] and Aciplex[®] are currently used as membranes in PEMFC's because of their excellent chemical stability, good mechanical properties and high proton conductivity characteristics. However, such polymers are very expensive and exhibit low operation temperature with high methanol permeability. Thus, current worldwide research focuses on the development of alternative hydrocarbon based polymer electrolyte membranes to overcome the drawbacks of Nafion[®] and its analogues.⁵

It is well known that thermoplastic engineering polymers with sulfonated groups introduced directly onto the polymer chain or pendant to the polymer backbone provides the following membrane characteristics which are required for an effective proton exchange membrane: (i) high proton conductivity; (ii) excellent oxidant and mechanical durability; (iii) reduced fuel permeability; (iv) low water uptake; (v) reduced swelling and good membrane fabrication properties and (vi) cost effectiveness. In particular, chemically and thermally stable, fully aromatic sulfonated poly(ether ether sulfone), sulfonated poly(ether ether ketone) and sulfonated polyimides are considered promising alternatives to Nafion[®] as the membrane material of choice in fuel cell technology.^{1,2,6-11}

Step-growth polymerization methods are generally employed for the preparation of a variety of thermoplastic engineering polymers. In general, poly(ether ether sulfone)s, poly(ether ether ketone)s and polyimides and its functionalized derivatives are readily prepared by reacting two or more different functionalized monomers via a step-growth polymerization process or by post-polymerization polymer backbone functionalization reactions to introduce the functional group pendant to the polymer chain.⁶

Poly(ether ether sulfone)s are tough, strong and stiff polymers with high chemical and thermal stability and are good polymer precursors for the preparation of membranes used in water purification processes, ultracentrifugation, reverse osmosis and liquid and gas separations.⁷ The most common methods for the preparation of poly(ether ether sulfone)s by the step-growth polymerization process involves three synthetic routes, namely:

- (a) the Friedel-Crafts reaction of different diaryl sulfone substrates with aromatic bissulfonylchlorides.⁶⁻⁸
- (b) the metal catalyzed coupling reaction of different silylated bisphenols with dihalogenated diaryl sulfones.⁶⁻⁸
- (c) the base mediated nucleophilic displacement reaction of aromatic bisphenols with activated dihalogenated diaryl sulfones.⁶⁻⁸

Poly(ether ether ketone)s are high performance polymers with excellent mechanical properties, good resistance to acidity and alkali and high thermal and thermoxidative stability.⁷ Poly(ether ether ketone)s are generally semi-crystalline polymers with limited solubility in common organic solvents. Poly(ether ether ketone)s are commonly prepared via the nucleophilic substitution reaction of dihalogenated diaryl ketones with aromatic bisphenol derivatives in the presence of a strong base as well as Friedel-Crafts carbonylation reactions.^{7,8} In addition, poly(ether ether ketone)s can also be prepared via metal catalyzed coupling reactions of different silylated bisphenols with dihalogenated diaryl ketones.^{7,8}

Polyimides are engineering thermoplastics with high thermal stability, good chemical resistance and excellent mechanical properties and are used in electronic packaging, passivation coatings, die attach adhesives, flexible circuit substrates and more recently as the interlevel dielectric in high speed IC interconnections.¹² In general, polyimides are prepared by the step-growth polymerization process via a two-step method. In the first step, the polyamic acid precursor is commonly prepared from the reaction of a tetracarboxylic dianhydride with an aromatic diamine via a ring-opening polycondensation reaction. In the

second step, the thermal or chemical cyclodehydration of the polyamic acid leads to the formation of the corresponding polyimide.⁹

The present study focuses on the synthesis of new engineering polymers based on 1,1diphenylethylene derivatives. A series of new poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives were prepared by step-growth polymerization methods by the reactions of different difunctionalized 1,1-diphenylethylene derivatives with dihalogenated diaryl sulfones, dihalogenated diaryl ketones and aromatic dianhydride as monomers respectively.^{13, 14} Poly(ether ether sulfone)s were prepared by the cesium fluoride or potassium carbonate catalyzed polymerization of dihalogenated diaryl sulfones with silylated bisphenols and bisphenols, respectively. Poly(ether ether ketone)s were prepared by the cesium fluoride catalyzed polymerization of dihalogenated diaryl ketones with silylated bisphenols. Polyimides were prepared via a two-step polymerization process which involves the formation of the polyamic acid derivative followed by a thermal imidization process. In addition, due to the regiospecific introduction of the 1,1-diphenylethylene unit along the polymer backbone in poly(ether ether sulfone)s, poly(ether ether ketone)s and polyimides, the new engineering polymers were subjected to a post-polymerization sulfonation process via a thiol-ene reaction¹⁵ to produce sulfonated poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives, respectively.

CHAPTER 2

LITERATURE REVIEW

2.1 Characteristics of Step-Growth Polymerization

2.1.1 **Polymer Structure**

The step-growth polymerization method is the major polymer synthesis process for the preparation of thermoplastic engineering polymers such as poly(ether ether sulfone)s, poly(ether ether ketone)s and polyimides.^{6-9, 16} In general, step-growth polymerization involves the reactions between different difunctional monomers which leads to the formation of polymer and the loss of molecule with low molecular weight, for example, in the preparation of polyesters and polyimides. However, step-growth polymerization reactions also occur when polymers are formed without elimination of small molecules, for example in the synthesis of polyurethanes and polyurea.^{12, 17-20} In most linear step-growth polymerization processes, the reactions are reversible. Thus, the final conversion and molecular weight is limited by the reaction equilibrium. When step-growth polymerization occurs with the loss of a molecule with low molecular weight, the concentration of the loss molecule considerably affects the reaction equilibrium. Consequently, the by-product needs to be removed to ensure the formation of polymers with high molecular weights. By removing the condensation by-

products, the rate of the reverse reaction is lowered and polymers with high molecular weights are produced.^{3, 17, 20}

Depending on the monomer structure, two types of linear step-growth polymerization methods are defined. One method involves the step-growth polymerization of two different difunctional monomers in which each monomer possesses only one type of functional group. The second method involves the polymerization of a single monomer containing two different functional groups.^{12, 19, 20} The two methods of polymers synthesis can be represented in general manner by the following equations:



where A and B are two different types of functional groups.

In the step-growth polymerization process, the monomers can react at any time in consecutive reactions leading to an increase of the molecular weight of the macromolecules. Therefore, no initiator is necessary. Catalysts, such as acids are commonly used to speed up and control the mechanism of the reaction. Monomers react progressively to form dimers, trimers until the formation of a polymer chain is obtained. Any two species in the reaction mixture can react with each other. The polymerization reaction proceeds with the number average molecular weight of the polymer increasing slowly throughout the reaction. Thus, the monomer concentration is rapidly reduced in the reaction. For most step-growth polymerization reactions, when the average polymer chains contain at least 10 monomers per unit, less than 1

percent of the original monomers remain present in the reaction mixture. Termination occurs when all available monomers are consumed.^{12, 19, 20} The step-growth polymerization reaction can be carried out by various techniques including melt polymerization, solution polymerization, interfacial polymerization, emulsion polymerization and solid state polymerization.³

2.1.2 Carothers' Theory

The mathematical expression leading to the manufacture of polymers with high molecular weights in step-growth polymerization reactions was developed by Wallace Carothers. In the Carothers equation, the degree of polymerization, X_n , is related to a given fractional monomer conversion, p, for a specific step-growth polymerization reaction. Polymers with high molecular weight are formed at high degrees of percentage monomer conversion or extent of reaction.¹⁹

For the linear step-growth polymerization method, the Carothers theory is depicted as follows:

$$A-A + B-B \rightarrow -(A-B)_n$$
-
Rate = k [A-A] [B-B]

The kinetic equation may be rewritten as:

Rate =
$$-d [A-A]/dt = k [A-A]^2 = k [B-B]^2$$

The degree of polymerization (X_n) and the number average molecular weight \overline{M}_n are given by the following equations:

$$X_n = N_0 / N_t$$
$$\overline{M}_n = M_0 \times X_n$$

With N_0 = number of functional groups present initially

 N_t = number of functional groups present at time t

 M_0 = value of the mean molar mass

 $M_0 = \frac{Molar \text{ mass of the repeat unit}}{Number \text{ of monomer units in the repeat unit}}$

The extent of reaction, p, in a given period of time is given by:

p = ______Number of carboxylic acid groups which have reacted Number of carboxylic acid groups initially present

The number of functional groups can be rewritten as:

 $p = (N_0 - N_t)/N_0$

Thus $X_n = 1/(1-p)$ [Carothers Equation]

2.1.3 Stoichiometric Control of Molecular Weight

The number average molecular weight of a specific polymer is one of the important polymer parameters which affect polymer properties such as glass transition and tensile strength.¹⁹ In

the step-growth polymerization process, the viscosity of polymer reaction in the melt and solution increases monotonically with molecular weight, making very high molecular weight polymers very difficult to process.⁶ Therefore, there is a need to deliberately control molecular weight in step-growth polymerization. There are three synthesis methods to purposefully control the molecular weight of a polymer in step-growth polymerization reaction,¹⁹ namely:

- (a) The reaction is quenched by a specific method at the appropriate time to avoid increase of molecular weight since the degree of polymerization is a function of reaction time.
- (b) The stoichiometry of the polymerization reaction is selected to have one monomer slightly in excess to avoid further polymerization. Polymerization stops when the monomer in smaller concentration is completely consumed and all chains have the same functional end groups (the functional group of the monomer in excess). The resulting polymer is stable to subsequent molecular weight changes, because further polymerization is impossible.
- (c) The polymerization reaction is controlled by the addition of a small amount of a monofunctional component. The monofunctional component is referred to as a chain stopper. The growing polymer produced does not possess functional end groups and is therefore incapable of further polymerization.

For a successful step-growth polymerization process and the production of polymers with high molecular weights, the following experimental requirements are essential:^{4, 6, 17}

- (a) A perfect stoichiometric equivalence of the two difunctional monomers.
- (b) High degree of purity of the monomers is necessary.

- (c) High monomer conversion (greater than 99 %).
- (d) Absence of side reactions to ensure high yield polymerization reactions.

2.1.4 Molecular Weight Distribution for Linear Step-Growth Polymerization

In step-growth polymerization, the product of polymerization is composed of macromolecules of different molecular weights. The broad molecular weight distribution is calculated considering that the reactivity of different functional groups is equal and independent of molecular size. Flory developed a statistical approach whereby the probability of finding a chain with x-structural units ("x-mer") that is equivalent to the probability of finding a molecule with (x-1) **A** groups reacted and one **A** group unreacted can be calculated as follows:¹⁹



The probability that an **A** functional group has reacted is given by p^{x-1} and the probability of finding an **A** unreacted is given by (1-p). Thus:

$$N_x = (1-p) p^{x-1}$$

where N_x = probability of finding a chain that is x-units long and has an unreacted **A**. When x increases, the probability decreases. Since N_x is the same as the mole or number fraction of molecules in the polymer mixture which are x-mers, the following equation can be written:

$$N_x / N = (1-p) p^{x-1}$$

where N = the total number of polymer molecules present in the reaction

If the total number of structural units present initially is N_0 , then $N = N_0(1-p)$. The equation N_x can be expressed as follows:

$$N_x = N_0 (1-p)^2 p^{x-1}$$

Similarly, the weight fraction of x-mers in the system and the probability of finding x-mers in terms of mass fraction is $W_x = x N_x / N_0$. The weight fraction of x-mers can also be rewritten as:

$$W_x = x (1-p)^2 p^{x-1}$$

2.1.5 Reaction Kinetics

To follow the polymerization kinetics for the step-growth polymerization reaction, it is assumed that there is equivalence in the reactivity of the two functional groups of the difunctional monomers, despite the size of the specific molecule or the extent of the reaction. The reaction rate constants of the step-growth polymerization process are completely independent of the reaction time and molecular weight of the polymeric species. The rate of step-growth polymerization is only expressed in terms of the concentrations of the reacting functional group. As a result, the polymerization rate decreases as the number of functional groups decreases.^{12, 19, 20}

The following parameters should be taken into consideration during the kinetic study of a step-growth polymerization reaction:^{19, 21}

- (a) The rate of polymerization can be expressed as the rate of disappearance of a specific functional group.
- (b) The concentration of a specific functional group is constant throughout the reaction.
- (c) Each step involves the reaction between one functional group with the other.
- (d) The reactivity of each functional group is independent of the chain length.

2.2 Engineering Polymers by Step-Growth Polymerization

2.2.1 Synthesis of Poly(ether ether sulfone)s

Aromatic poly(ether ether sulfone)s is a family of thermoplastic polymers containing the sub unit with the aryl-SO₂-aryl functionality. Poly(ether ether sulfone)s, first introduced in 1965 by Union Carbide, possess excellent mechanical, biological and chemical stability with an extensive operating range of temperatures (>80 °C) and pH values. The unique chemical and physical characteristics of poly(ether ether sulfone) make it the polymer material of choice for membrane substrates in fuel cell technology and water purification processes.^{6-8, 19, 20} Poly(ether ether sulfone)s are inexpensive and commercially available. Udel[®] is one typical example of a commercially available poly(ether ether sulfone):



In particular, aromatic poly(ether ether sulfone)s are well-known high performance engineering polymers with good thermal stability and good mechanical properties because of the incorporation of aromatic nuclei along the polymer backbone. In addition, the presence of the flexible ether linkages along the polymer backbone facilitates polymer processing while maintaining excellent oxidative and thermal properties. The synthesis of a plethora of different poly(ether ether sulfone) derivatives with different polymer backbone chemical composition and microstructure have been reported in the literature.^{6, 7}

The general synthesis methods for the preparation of different poly(ether ether sulfone)s involve electrophilic aromatic substitution, metal catalyzed coupling reaction and nucleophilic aromatic substitution mechanisms.^{6, 7, 22}

2.2.1.1 Poly(ether ether sulfone)s by Electrophilic Aromatic Substitution Reactions

The electrophilic aromatic substitution polycondensation process was the first method used for the synthesis of poly(ether ether sulfone)s. Poly(ether ether sulfone)s were prepared by the Friedel-Crafts polysulfonylation reaction of an arylene sulfonyl chloride derivative with an aromatic compound in the presence of a Lewis acid catalyst.⁶ A sulfonium ion, generated from an arylene sulfonyl chloride and Lewis acid, attacks the aromatic compound and leads to the formation of para substituted linear polymers.^{23, 24} Two different routes^{6, 7, 19, 20} are employed for the synthesis of poly(ether ether sulfone)s via the Friedel-Crafts

polysulfonylation reaction, namely (a) the reaction of two different polyfunctional monomers of the AA and BB type and (b) the polymerization of monomers of the AB types:



2.2.1.2 **Poly(ether ether sulfone)s by Metal Catalyzed Coupling Reactions**

The synthesis of poly(ether ether sulfone)s can also be effected by the metal catalyzed coupling reactions of dihalogenated diaryl sulfones with silylated bisphenols with cesium fluoride or potassium fluoride as catalyst.^{6,7} For example, the treatment of 4,4′-difluorodiphenylsulfone with silylated bisphenol A in the presence of CsF in tetrahydrofuran produces the corresponding poly(ether ether)sulfones in high yields:⁷



The fluoride anion from the catalyst converts the silyl ether to phenolate salt derivative. The phenolate salt species attack the dihalide monomer to produce the polymer. The use of silylated ethers of bisphenols allows the preparation of poly(ether ether sulfone)s in the melt (temperatures between 130 - 300 °C) in the presence of 0.1 - 0.3 % mol of catalyst, thus avoiding the removal of large amounts of inorganic salts and solvents. However, the metal catalyzed coupling method is limited only to the use of fluorinated monomers, with chlorinated monomers affording polymers with low molecular weights.^{6, 7, 16, 20, 22, 25}

Another metal catalyzed synthesis method for poly(ether ether sulfone)s involves the Ni(0) homocoupling reactions of the appropriate aromatic ether sulfone dihalides.^{26, 27} The method was first developed for the synthesis of soluble functionalized poly(*p*-phenylene)s (PPP) and polyarenes derivatives from substituted dichlorobenzene and triflates of hydroquinones and bisphenols.²⁶⁻²⁸ The Ni(0) catalyst is generated by the reduction reaction of NiCl₂ with Zn in the presence of triphenylphosphine and bipyridine in N,N-dimethylacetamide to reduce potential side reactions such as the reduction of ArCl to ArH and the transarylation of triphenylphosphine:²⁹



The current research work focuses on the synthesis of new poly(ether ether sulfone)s via the metal catalyzed polymerization of dihalogenated diaryl sulfones with silylated bisphenols. The polymerization reaction of 4,4'-difluorodiphenylsulfone (**1**) with different percentage mole ratios of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) and 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) afforded well-defined poly(ether ether sulfone) derivatives in high yields.

2.2.1.3 Poly(ether ether sulfone)s by Base Catalyzed Nucleophilic Aromatic Substitution Reactions

The aromatic nucleophilic substitution polycondensation reaction between aromatic dihalides and aromatic diols can be employed to produce engineering polymers via step-growth polymerization process.^{30, 31} For example, the nucleophilic aromatic substitution polycondensation reaction of 4,4'-difluorodiphenylsulfone with bisphenol A affords poly(ether ether sulfone)s in high yields. A weak base, K_2CO_3 is used as catalyst to afford the bisphenolate in the first step. Potassium carbonate serves as catalyst and HF acceptor. Toluene is added as co-solvent for the azeotropic removal of the liberated water.²⁵ In the second step, the bisphenolate reacts with the dihalide monomer to yield the resultant poly(ether ether sulfone) derivative. The nucleophilic displacement polycondensation of the aromatic dihalide and the bisphenol is carried out in aprotic polar solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc) or dimethylsulfoxide (DMSO) as solvent to provide a plethora of poly(ether ether sulfone)s derivatives with different backbone structures.^{6,7,21,25,29,32,33}

Gao and Hay³³ prepared a series of poly(ether ether sulfone)s containing the diphenylethylene unit via the base catalyzed aromatic nucleophilic substitution polycondensation reaction of 4,4´-difluorodiphenylsulfone with 1,1-bis(4-hydroxyphenyl)ethylene in DMAc and toluene as solvent to produce well-defined polysulfones for use as precursors in photochemical reactions:



McGrath and coworkers³⁴ have investigated the kinetics and mechanism associated to the synthesis of poly(ether ether sulfone)s using K_2CO_3 /DMAc as base and aprotic dipolar solvent. Several homopolymers and copolymers of 4,4⁻-dichlorodiphenylsulfone and 4,4⁻-difluorodiphenylsulfone with bisphenol A, bisphenol T, bisphenol S and hydroquinone were

prepared in different monomer mole ratios to produce polymers with high molecular weights. In addition, polymer hydrolysis and bisphenate insolubility, usually observed in the synthesis of poly(ether ether sulfone)s via the classical synthetic route using sodium hydroxide and DMSO system, were avoided:



In the present study, the base catalyzed nucleophilic substitution reaction of dihalogenated diaryl sulfones with bisphenols was adopted for the preparation of new poly(ether ether sulfone) derivatives with the 1,1-diphenylethylene unit incorporated along the polymer backbone. The potassium carbonate catalyzed polymerization of 4,4'-difluorodiphenylsulfone (1) with different mole percentage ratios of bisphenol A (4) and 1,1-bis(4-hydroxyphenyl)ethylene (5) afforded a series of new well-defined poly(ether ether sulfone) derivatives with excellent chemical and thermal stability.
2.2.2 Synthesis of Sulfonated Poly(ether ether sulfone)s

The synthesis of new sulfonated high performance polymers is widely considered as the replacement for Nafion[®] as the polymer electrolyte membrane in fuel cell technology. Nafion[®] is a sulfonated tetrafluoroethylene based copolymer utilized in proton exchange membrane fuel cells and direct methanol fuel cells to transfer protons from the anode to the cathode, thus providing a barrier between electrodes. However, Nafion[®] have limited use due to their high cost, low temperature operation (\leq 80 °C), propensity for dehydration, high methanol crossover and environmental recycling problems.¹⁻³ Thus, to replace Nafion[®] as the polymer substrate in PEMFCs, many sulfonated engineering polymers based on poly(ether ether sulfone) have been prepared by the incorporation of sulfonic acid groups into the polymer backbone.⁵ In general, sulfonated poly(ether ether sulfone)s can be prepared by three general methods, namely:

- (a) The direct copolymerization of sulfonated monomers.
- (b) The direct post-polymerization sulfonation reactions.
- (c) The post-polymerization sulfonation reaction to introduce the sulfonic acid group pendant to the polymer chain.

2.2.2.1 Sulfonated Poly(ether ether sulfone)s by Direct Copolymerization of Sulfonated Monomers

Sulfonated poly(ether ether sulfone)s can be prepared by the step-growth polymerization reaction of an appropriate difunctionalized monomer with a sulfonated difunctionalized

monomer. In general, the sulfonated difunctionalized monomer can be prepared by electrophilic aromatic substitution reaction of difunctionalized monomer with an appropriate sulfonating agent. Many research groups outlined the preparation of sulfonated monomers with different degrees of purity from the reactions of 4,4′-dichlorodiphenylsulfone with different sulfonating agents.³⁵⁻⁴² The synthesis of a sulfonated dihalogenated diaryl sulfone monomer widely used in step-growth polymerization reactions was first reported by Robeson and Matzner.³⁵ McGrath and coworkers³⁶ and Ueda and coworkers³⁷ also reported the preparation and purification of sulfonated 4,4′-dichlorodiphenylsulfone used in condensation polymerization. McGrath and coworkers³⁸ reported the synthesis of sulfonated monomers from 4,4′-dichlorodiphenylsulfone using the method of Ueda and coworkers,³⁷ with modifications.



The principal advantage of preparing sulfonated poly(ether ether sulfone)s by the base catalyzed nucleophilic aromatic substitution copolymerization of sulfonated monomers is the control of the sulfonation content and site of sulfonation during the step-growth polymerization process.^{43, 44} For example, Zhang and coworkers⁴⁵ prepared a novel series of bisphenol A based sulfonated poly(arylene ether sulfone) by the base catalyzed nucleophilic aromatic copolymerization of bisphenol A with 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone and 4,4′-dichlorodiphenylsulfone. The different sulfonated poly(arylene ether sulfone) samples were evaluated as polymeric candidates for PEM in direct methanol fuel cells:



Yoon and coworkers⁴⁶ reported the synthesis of a new sulfonated poly(ether ether sulfone) from 3,3'-disulfonated-4,4'-difluorodiphenylsulfone (SDFDPS) and investigated the effect of the membrane properties of the resultant sulfonated polymers. Sulfonated poly(ether ether sulfone) were prepared by nucleophilic aromatic polymerization reaction of 1,6-bis(4fluorophenyl)-perfluorohexane (FPPFH), 6F-bisphenol A (6F-BPA) with SDFDPS using K_2CO_3 as catalyst. The reaction was performed at 150 °C in the presence of NMP and toluene as solvents:



2.2.2 Sulfonated Poly(ether ether sulfone)s by Post-Polymerization Sulfonation Methods: Direct Sulfonation

The most common method for the sulfonation of aromatic poly(ether ether sulfone)s via postpolymerization methods involves the classic electrophilic aromatic substitution reaction whereby the hydrogen atom of the aromatic ring is replaced by an electrophile using different sulfonating agents. Sulfonation takes place on the aromatic ring of the phenyl ether ring due to the electron-withdrawing inductive and resonance effects of the SO₂ group.⁴⁷ The following sulfonating agents have been employed in the sulfonation of poly(ether ether sulfone) derivatives by electrophilic aromatic substitution mechanisms:^{6, 11, 48-56}

Sulfonating agents	Reactivity	Comments
Chlorosulfonic acid	High	Inexpensive, side reactions
		(degradation, crosslinking)
Fuming H_2SO_4 oleum	High	Inexpensive, crosslinking
H_2SO_4	High	Inexpensive, lowering of reactivity by
		reaction product (water)
SO ₃ / Triethyl phosphonium	Medium to high	Inexpensive
Trimethylsilylsulfonyl	Medium	Relatively expensive
chloride		
Acetylsulfate	Low	Inexpensive
$BuLi+SO_2 \text{ or } SO_3$	High	Expensive
BuLi+ Sultones,	High	Expensive
Halogenoalkyl sulfonic acid		

For example, Smitha and coworkers⁴⁹ prepared sulfonated poly(ether ether sulfone)s from the reaction of commercially available poly(ether ether sulfone) with chlorosulfonic acid and the sulfonated derivative was evaluated as the polymer substrate for membranes in fuel cell applications. Due to the electron withdrawing sulfonic acid groups on the ortho ethers sites, the hydrolytic stability of the ether linkage was reduced and chain degradation and crosslinking reactions were observed when chlorosulfonic acid was used as sulfonating agent.⁴⁸



Sulfonation of commercially available poly(ether ether sulfone)s with chlorotrimethylsilyl sulfonate at room temperature proceeded without side reactions due to the lower electrophilicity of chlorotrimethylsilyl sulfonate. The degree of sulfonation was controlled by varying the reaction time and mole ratio of the sulfonating agent to the polymer.⁴⁷ However, the most efficient sulfonation reaction for poly(ether ether sulfone)s involves the use of sulfonating agents based on SO₃, such as SO₃/dichloromethane and SO₃/triethylphosphate complex.^{49, 53} Noshay and Robeson⁵³ prepared sulfonated poly(ether ether sulfone) from the reaction of commercially available Udel[®] with sulfur trioxide and triethylphosphate. The introduction of $-SO_3Na$ groups onto the poly(ether ether sulfone) backbone increases the glass transition temperature due to the increased intermolecular associations via the polar ionic sites:



2.2.2.3 Sulfonated Poly(ether ether sulfone)s by Post-Polymerization Sulfonation Methods: Sulfonation Pendant to the Polymer Chain

A regiospecific, well-controlled chemical modification reaction of poly(ether ether sulfone) was developed by Guiver⁵⁷ and exploited by Summers⁵⁸ and Jannasch and coworkers⁵⁹ for the regiospecific introduction of functional groups on the polymer backbone.⁵⁹⁻⁶² The reaction involves the lithiation of the polysulfone precursor and the subsequent reaction of the lithiated polysulfone derivatives with the appropriate electrophilic species. For example, Jannasch and coworkers⁵⁹ reported the reaction of lithiated poly(ether ether sulfone)s with 4-fluorobenzoyl chloride in the first step, followed by the sulfonation of reaction via the base catalyzed substitution of the fluorine atom with either 4-sulfophenoxy or 7-sulfo-2-naphtoxy units to afford the corresponding sulfonated poly(ether ether sulfone) derivatives:



Another method for the preparation of functionalized engineering polymers with the functional group pendant to the polymer backbone involves the use of thiol-ene click chemistry.^{15, 63, 64} Functionalized thiols can be used to form a sulfur linkage with polymers containing some degree of insaturation by the thiol-ene free radical coupling reaction with the resultant introduction of the functionalized group pendant to the polymer backbone.¹⁵ In a reaction which involves the hydrothiolation of a C=C bond, the thiol-ene reaction can occur via a photochemically and radical-mediated method, nucleophile-mediated method, acid/base catalysis and solvent promoted process.^{15, 47, 63-73} For example, Jannasch and coworkers,⁷⁴ exploited the thiol-ene synthetic strategy for the preparation of functionalized poly(ether ether sulfone). First, the undecenoyl side chain was introduced onto the poly(ether ether sulfone) backbone by the reaction of the lithiated polysulfone derivative with undocenoyl chloride in THF at -40 °C. Treatment of the undecenoyl functionalized polysulfone derivative with 2-(2benzimidazolyl)ethanethiol in the presence of 2,2'-azobis(isobutyronitrile) (AIBN) gave the poly(ether ether sulfone) with the introduction of the benzimidazole moiety pendant to the polymer chain:



The current research work utilizes the thiol-ene click reaction for the introduction of the sulfonate group pendant to the polymer backbone. Due to the regiospecific introduction of the 1,1-diphenylethylene unit along the polymer backbone, the thiol-ene free radical coupling

reaction of poly(ether ether sulfone) with sodium 3-mercapto-1-propane sulfonate and AIBN affords sulfonated poly(ether ether sulfone) with the sulfonate group pendant to the polymer backbone.

2.2.3 Synthesis of Poly(ether ether ketone)s

Poly(ether ether ketone)s (PEEK) are semicrystalline thermoplastic polymers with the combined chemical characteristics of the ether and ketone groups. The first poly(ether ether ketone), named Victrex[®], was prepared by Bonner at DuPont in 1962 via the Friedel-Crafts acylation reaction.⁷⁵ Poly(ether ether ketone)s have low smoke and toxic gas emissions and low moisture absorption, with high mechanical strength and excellent chemical resistance.⁶⁻⁷ The mechanical and chemical resistance of poly(ether ether ketone)s are retained at high temperature, including continuous service temperature of 260 °C. Poly(ether ether ketone)s are used in the aerospace, automotive, marine, nuclear, oil-well, electronics, medical and chemical and chemical and have the following general structure:^{6,7, 19-21}



A large variety of poly(ether ether ketone)s with different chemical structures and polymer properties can be prepared by standard organic chemistry reactions. The synthesis of poly(ether ether ketone)s can be achieved via electrophilic aromatic substitution reactions, metal catalyzed coupling reaction mechanisms and nucleophilic aromatic substitution reactions.^{6, 7, 21}

2.2.3.1 Poly(ether ether ketone)s by Electrophilic Aromatic Substitution Reactions

The Friedel-Craft acylation reaction was used by Bonner⁷⁵ for the synthesis of the first poly(ether ether ketone).⁶ The step-growth polymerization reaction involves the treatment of diphenylether with terephthaloyl chloride in nitrobenzene solution in the presence of a catalyst such as aluminium chloride:



Different poly(ether ether ketone)s with high molecular weight have been prepared by Friedel-Craft acylation methods using different monomers, solvents and reaction conditions.^{6, 7, 22, 44, 59, 76} For example, Joshi and coworkers⁶⁰ prepared poly(ether ether ketone) copolymers from the reaction of o-chloroanisole with 1,4-phenylenedioxy diacetylchloride (1,4-PDC) and appropriate dihalides using anhydrous AlCl₃ as catalyst and CS₂ as solvent by Friedel-Craft acylation and alkylation reactions, respectively.



With R = $-CH_2$; $-CH_2$ $-CH_2$

The resultant polymers with low molecular weights were tested for biological activities against bacteria, fungi and yeast due to the presence of chlorine within the polymer backbone.

Rose⁷⁷ reported the synthesis of poly(ether ether ketone) from a carboxylic acid derivative with an activated phenyl ether moiety using trifluoromethanesulfonic acid as catalyst to form polymers with high molecular weights:



2.2.3.2 Poly(ether ether ketone)s by Metal catalyzed Coupling Reactions

The utilization of the metal catalyzed coupling reaction in polymerization processes provides an efficient method for the preparation of poly(ether ether ketone)s with high molecular weights. For example, Kricheldorf and Bier⁷⁸ prepared well-defined poly(ether ether ketone) derivatives by the reaction of the appropriate dihalogenated diaryl ketone derivatives with specific silvlated bisphenols using cesium fluoride as catalyst in a metal catalyzed coupling solution or melt polymerization reaction.^{6,7,22} For example, treatment of 4.4'difluorobenzophenone with different silvlated bisphenols such as silvlated bisphenol-A, tetramethylbisphenol-A, 1,1-bis(4-hydroxyphenyl)cyclohexane and 4,4'dihydroxydiphenylsulphone in the presence of cesium fluoride afforded well-defined poly(ether ether ketone)s in high yields. The activated cesium phenoxide is generated with cesium fluoride as the catalyst. The effectiveness of the catalyst depends on the formation of dissolved fluoride ions which cleave the Si-O bond of silvlated bisphenol derivatives. The fluoride ions are highly nucleophile and attack the Si-O bond to generate a more stable Si-F bond.⁷⁸ The volatile by-product, trimethylsilyl fluoride is removed at high temperature. The polymer products were isolated in its pure form, thus avoiding the process of removal of inorganic salts and solvents. For example:

33



Emrick and coworkers⁷⁹ prepared a series of new poly(ether ether ketone) derivatives by the cesium fluoride catalyzed polymerization of dihalogenated diaryl ketones with silylated derivatives of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (BPC) and bisphenol A (BPA):



Similarly, in the current study, a series of new poly(ether ether ketone) derivatives were prepared by the cesium fluoride catalyzed polymerization of 4,4⁻-difluorobenzophenone (6) with 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (2) and

1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) in different mole ratios of monomers to afford well-defined poly(ether ether ketone) derivatives with the regiospecific introduction of the 1,1-diphenylethylene unit along the polymer backbone.

2.2.3.3 Poly(ether ether ketone)s by Base Catalyzed Nucleophilic Aromatic Substitution Reactions

Poly(ether ether ketone)s can also be prepared by nucleophilic aromatic substitution reactions using appropriate aromatic dihalogenated ketones and diphenolates as monomers. Potassium carbonate or sodium carbonate is used as the catalyst and the polymerization reaction is conducted in aprotic solvents.^{6,7, 80} Johnson and coworkers⁸¹ were the first to prepare poly(ether ether ketone) by step-growth polymerization via nucleophilic aromatic substitution mechanisms using appropriate dihalogenated diaryl ketones and diphenolates in the presence of sodium hydroxide as catalyst and DMSO as solvent. However, poly(ether ether ketone)s obtained were insoluble in DMSO. To overcome the polymer solubility problem, the careful choice of solvent resulted in facile step-growth polymerization reactions to form polymers with high molecular weights.⁶⁻⁷ For example, the step-growth polymerization reaction of 4,4′- difluorobenzophenone with the disodium salt of hydroquinone in the presence of sodium carbonate and diphenylsulphone (DPS) as solvent at 300 °C afforded poly(ether ether ketone)s in a nucleophilic aromatic substitution polycondensation reaction.^{7, 22} The carbonyl electron

withdrawing group is necessary to activate the aromatic dihalides. The leaving group should be a fluoride ion to afford polymers with high molecular weights:²²



Koch and Ritter⁸² prepared a series of new aromatic poly(ether ether ketone)s via the base catalyzed nucleophilic aromatic substitution reactions of 4,4'-difluorobenzophenone with bisphenol A and 4,4-bis(4-hydroxyphenyl)pentanoic acid. Well-defined poly(ether ether ketone) derivatives were obtained and DSC analyses data show that amorphous polymers were obtained with the glass transition temperatures increasing with the content of the acidic monomer:



The direct synthesis of poly(ether ether ketone)s in solution by nucleophilic aromatic substitution reactions results in the formation of polymers with low molecular weights due to inherent solubility problems. However, the solubility of the resultant polymer can be increased by using functionalized bisphenol derivatives as monomers, followed by the step-growth polymerization process to form polymers with high molecular weights after the final removal of the substituent group. For example, Risse and Sogah⁸³ prepared poly(ether ether ketone) with high molecular weights via (a) the base catalyzed nucleophilic substituted aromatic diol in solution to provide a soluble, amorphous substituted poly(ether ether ketone) derivative, and (b) followed by removal of the substituent group by retro-Friedel-Crafts alkylation in the presence of a Lewis acid (CF_3SO_3H) to give the final crystalline poly(ether ether ketone):



Another route for the preparation of poly(ether ether ketone)s via a soluble precursor was developed by Mohanty and coworkers.⁸⁴ The base catalyzed nucleophilic substitution polycondensation reaction of a Schiff base of a dihalogenated diaryl ketone derivative with an appropriate aromatic bisphenol at low temperature gave a polyketimine derivative, which was subsequently converted to poly(ether ether ketone)s using HCl as catalyst:



2.2.4 The Synthesis of Sulfonated Poly(ether ether ketone)s

Sulfonated poly(ether ether ketone)s (SPEEK) have been utilized as the polymer substrate for the formation of membranes in ultrafiltration processes and as nanocomposite proton exchange membranes in fuel cell technology.¹⁸ In general, sulfonated poly(ether ether ketone)s can be prepared by three synthetic methods namely:

(a) The direct copolymerization reactions of sulfonated monomers with appropriate monomers.

- (b) The direct post-polymerization sulfonation reactions with poly(ether ether ketone) derivatives.
- (c) Sulfonation reactions of poly(ether ether ketone)s to introduce the sulfonate group pendant to the polymer chain.

2.2.4.1 Sulfonated Poly(ether ether ketone)s by Direct Copolymerization of Sulfonated Monomers

Random (statistical) sulfonated poly(ether ether ketone)s can be obtained by the direct copolymerization of an appropriate dihalogenated diaryl ketone or diaryl ether monomer unit with a specific sulfonated dihalogenated diaryl ketone monomer or sulfonated bisphenol derivative.^{6, 7} The step-growth copolymerization reaction using sulfonated monomers results in the regiospecific introduction of the sulfonate group along the polymer backbone and the sulfonation sites and sulfonation content can be controlled by the careful control of the reaction stoichiometry.^{6,7}

Sulfonated dihalogenated diaryl ketone or bisphenol monomer derivatives can be prepared by electrophilic aromatic substitution reactions using different sulfonating agents:^{22, 85-91} For example, Koji and coworkers⁹² reported the synthesis of a sulfonated dihalogenated diaryl ketone monomer by the treatment of 4,4′-difluorobenzophenone with 25.3 % fuming sulfuric acid to afford disodium-3,3′-disulfate-4,4′-difluorobenzophenone in 100 % yield and high purity.



A series of sulfonated poly(ether ether ketone)s were prepared by the base catalyzed nucleophilic aromatic polycondensation reaction of 4,4⁻-difluorobenzophenone and pure sulfonated monomer, disodium-3,3⁻-disulfate-4,4⁻-difluorobenzophenone with hexafluoroisopropylidene diphenol.⁹³ Polymers with high molecular weights were obtained which are thermally stable up to 260 °C. The resultant sulfonated poly(ether ether ketone)s were employed as proton exchange membranes in fuel cells applications:





2.2.4.2 Sulfonated Poly(ether ether ketone)s by Post-Polymerization Sulfonation Methods: Direct Sulfonation

Poly(ether ether ketone)s are high performance polymers that are insoluble in most organic solvents. However, the incorporation of the sulfonic acid group along the polymer backbone of poly(ether ether ketone)s leads to a decrease in crystallinity and an increase in the solubility of the resultant polymer.³⁷ In general, the direct sulfonation of poly(ether ether ketone)s using different sulfonating agents is not regiospecific because of the lack of control of the degree and site of sulfonation during the sulfonation process.³⁷ In addititon, polymer degradation and numerous side reactions are observed. Sulfonation of poly(ether ether ketone)s by sulfonating agents such as H₂SO₄ proceeds via the electrophilic substitution reaction mechanism. The phenyl rings of the polymer chain are activated for the electrophilic substitution reactions by the ether linkage and the sulfonating group is introduced into the hydroquinone segment of the polymer chain.^{94, 95} One sulfonic acid group is generally added per unit due to the electronattracting nature of the carbonyl group which makes the electron density of the other aromatic rings very low.^{37,95} However, at higher temperature or long reaction times, disulfonation reactions are possible.⁹⁵ In general, sulfonation reactions with poly(ether ether ketone)s are conducted in the presence of chlorosulfonic acid^{94, 96, 97} or sulfuric acid as sulfonating agents.^{97, 98-100} Sulfonation with sulfuric acid is a heterogenous reaction controlled by the reaction time, temperature and acid concentration.^{97, 98} For example, Javaid Zaidi¹⁰⁰ prepared sulfonated poly(ether ether ketone) from Victrex and 97.5 % concentrated sulfuric acid at room temperature at different reaction times to produce polymers of different degrees of

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sulfonation. The sulfonated poly(ether ether ketone) derivatives were employed as electrochemical devices in fuel cell and electrodialysis processes:



2.2.4.3 Sulfonated Poly(ether ether ketone)s by Post-Polymerization Sulfonation Methods: Sulfonation Pendant to the Polymer Chain

Standard organic reactions are commonly employed for the functionalization of poly(ether ether ketone)s to facilitate the introduction of the sulfonic acid group pendant to the polymer chain. The reactive sites along the polymer chain can be introduced directly along the polymer backbone or by the introduction of an appropriate functional group pendant to the polymer chain in the polymer precursor prior to the sulfonation functionalization reaction. For example, Zhu and coworkers¹⁰¹ prepared a series of new sulfonated poly(ether ether ketones) using dihydroxy functionalized poly(ether ether ketone)s as substrates. The synthesis of dimethoxylnaphthalene based poly(ether ether ketone) derivative was conducted by the base catalyzed nucleophilic aromatic substitution polymerization method and the subsequent demethylation reactions afforded the corresponding dihydroxynaphthalene based poly(ether ether ketone) derivative. The preparation of sulfonated poly(ether ether ketone) was effected by the base catalyzed nucleophilic reaction of the dihydroxynaphthalene based poly(ether ether ketone) with 1,4-butane sultone via a ring-opening mechanism. The resultant sulfonated poly(ether ether ketone) derivative with pendant sulfonic acid groups exhibits high proton conductivity in DMFC applications:



Another synthetic route for the preparation of sulfonated poly(ether ether ketone)s with the sulfonic acid group pendant to the polymer chain was developed by Tsai and Lin.¹⁰² The synthesis method involves the reaction of poly(ether ether ketone) with concentrated sulphuric acid, followed by the treatment of the resultant sulfonated poly(ether ether ketone) with 1,1′- carbonyl-diimidazole (CDI) to afford pristine sulfonated poly(ether ether ketone). Subsequent reaction with 2-aminoethanesulphonic acid afforded novel main-chain type and side-chain type sulfonated poly(ether ether ketone) with improved nano-phase separation morphology. The introduction of the new sulfonated group pendant to the polymer chain accounted for the formation of well-defined nano-phase separation morphology and enhanced the characteristics of the proton exchange membrane in DMFC applications:



The sulfonic acid group can also be introduced pendant to the poly(ether eher ketone) chain via the thiol-ene reaction which involves the following procedure:

- (a) The preparation of the poly(ether ether ketone) precursor derivative bearing a site of unsaturation pendant to the polymer chain.
- (b) The reaction of the pendant site of unsaturation with a mercapto compound bearing the sulfonate group via the classic thiol-ene reaction.

Guan and coworkers¹⁵ used the thiol-ene method for the synthesis of poly(aryl ether ketone) ionomers with sulfonic acid groups pendant to the polymer backbone: Treatment of the propenyl derivative of poly(ether ether ketone) with sodium 3-mercapto-1-propane sulfonate and AIBN in NMP/DMSO produced sulfonated poly(ether ether ketone) in quantitive yields. The sulfonated poly(ether ether ketone)s were used as polymeric membrane substrates for fuel cell technology applications:



The current research work outlines a new synthesis route for the preparation of sulfonated poly(ether ether ketone)s using the thiol-ene reaction to introduce the sulfonate group pendant to the polymer backbone. Treatment of a new poly(ether ether ketone) derivative, with the 1,1-diphenylethylene unit regiospecifically introduced in the polymer backbone, with sodium 3-mercapto-1-propane sulfonate and AIBN afforded the corresponding well-defined sulfonated poly(ether ether ketone).

2.2.5 Synthesis of Polyimides

Polyimides are engineering polymers with high thermal stability, excellent oxidative stability, good mechanical properties and are used in high performance applications in the electronics and aerospace industries.^{6,9} Initially, aromatic polyimides were prepared by the melt polymerization of diamines and tetracids or diacid/diesters derivatives. However, such polymers were intractable and difficult to process.⁹ The first high molecular weight aromatic polyimides were prepared by researchers at the DuPont Chemical Company by the polycondensation reactions of pyromellitic acid (1,2,4,5-benzenetetracarboxylic dianhydride) and aliphatic diamines¹⁰³ with the following the general structure. For example:



$$R = -(CH_2)_{3} C(CH_2)_{3} C(CH_2)_{3}$$

2.2.5.1 The Synthesis of Polyimides via a Three Step Process

The synthesis of polyimides can occur by a three step process which involves the formation of intermediate polyisoimides, an isomeric form of polyimides.⁹ In the three step process, the polyamic acid intermediate is prepared in the first step from the polycondensation reaction between an appropriate dianhydride and a diamine at room temperature. In the dehydration step, the resultant polyamic acid is then converted to polyisoimides by treatment with dicyclohexyl carbodiimide (DCC) or trifluoroacetic anhydride as dehydrating agents. In the final step, the polyisoimides are converted to the corresponding polyimides by heating at high temperature.¹⁰⁴⁻¹⁰⁶ For example, Oh and coworkers¹⁰⁷ reported the synthesis of polyimides from polyisoimides using 4,4′-oxydiphthalic anhydride (ODPA) and 4,4′-oxydianiline (ODA) as starting material:



2.2.5.2 The Synthesis of Polyimides via a Two Step Process

Polyimides are commonly prepared via a two step process using tetracarboxylic dianhydrides and diamines as substrates.¹⁰⁴ In the first step, the polycondensation reaction between an appropriate aromatic tetracarboxylic dianhydride and an appropriate aromatic diamine at room temperature in a polar aprotic solvent affords a polyamic acid derivative via a ring-opening polycondensation reaction. The second step involves the imidization process via the thermal or chemical cyclodehydration reaction of the polyamic acid. At room temperature, polyamic acid is formed when an appropriate dianhydride is treated with a specific diamine in the presence of a polar aprotic solvent such as DMAc. Polyamic acids with high molecular weight are produced in an equilibrium reaction. At high monomers concentrations, the formation of polyamic acids with high molecular weights is favoured. The reaction mechanism involves the nucleophilic attack of the amino group of diamine derivative on the carbonyl carbon of the dianhydride followed by the opening of the anhydride ring to form the amic acid group.^{6,7,9} The polyamic acid can then undergo a thermal cyclodehydration reaction at 200 - 300 °C to form the imide ring with concomitant removal of the water byproduct. The high degree of imidization (as high as 99 %) can be achieved at 230 - 250 °C for 10 minutes. Polyamic acids in the film form promote the imidization reaction.⁹

The thermal imidization reaction which involves the cyclodehydration of polyamic acid is widely used in the industry and is suitable for the preparation of thin objects such as films, coatings, fibers and powders in order to allow the diffusion of by-product and solvent without forming bristle and voids in the final polyimide product.^{104, 108}

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The chemical imidization reaction by the cyclodehydration of the polyamic acid is carried out at room temperature by treatment of the polyamic acid solution with a suitable mixture of dehydrating agents, such as acetic anhydride and pyridine. High degrees of imidization are usually obtained by the chemical imidization process.^{9, 109-113} Ye and coworkers¹¹⁰ outlined the preparation of polyimides by polycondensation reactions between five different dianhydrides, (2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA), 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA), 4,4'-

(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA) and 4,4'-oxydiphthalic anhydride (ODPA)) with 2,2-bis[4-(4aminophenoxy)phenyl]hexafluoropropane as precursors. The process involves a two step polyimide synthesis method which involves the formation of the polyamic acid intermediate and the subsequent chemical imidization reaction at ambient temperature to form the resultant polyimide derivative:



Wang and coworkers,¹¹¹ prepared different polyimides via a two step process polymerization method by the polycondensation reactions of 4-phenyl-2,6-bis[4-(4-aminophenoxy)-phenyl]pyridine with equimolar amounts of different aromatic dianhydrides in N-methyl-2-pyrrolidone. The polyamic acid intermediates were converted to the corresponding polyimide derivatives by a thermal imidization process or a chemical imidization method using acetic anhydride/pyridine. Processable polyimides were prepared with good solubility in polar aprotic solvents:



Soluble polyimides can also be prepared by a two step polyamide synthesis process which involves derivatives such as polyamic acid alkyl esters and polyamic acid trimethylsilyl esters.^{104, 114} For example, Becker and Schmidt¹¹⁵ described the conversion of several paralinked aromatic polyamic acid alkyl esters precursors to the corresponding aromatic polyimides. The esters were prepared by the polycondensation of bis(alkoxycarbonyl)substituted aromatic dicarboxylic acids derived from tetracarboxylic dianhydrides and
alcohols or their acid chlorides with aromatic primary diamines. The polyamic acid alkyl esters were heated to afford polyimides with the concomitant elimination of alcohols:



De la Campa and coworkers¹¹⁶ also reported the preparation of polyimides via the two step polyimide synthesis process which involves polyamic acid trimethylsilyl esters as intermediates. The intermediate trimethylsilyl esters derivatives were prepared from the reaction of N-trimethylsilyl-substituted aromatic secondary diamines with tetracarboxylic dianhydrides via a ring–opening polycondensation reaction. Subsequent thermal imidization led to the lost of trimethylsilanol and formation of the resultant polyimides:



In the present study, a series of new polyimides were prepared via a two process polyimide synthesis process from the reactions of 4,4'-oxydiphthalic anhydride (7) with different mole percentage ratios of 2,2-bis[4-(4-aminophenoxy)phenyl]propane (8) and 1,1-bis(4-aminophenyl)ethylene (9). The polyamic acid intermediates were produced at room temperature after 24 hours and were cast on a glass plate and then subjected to a thermal imidization process for 3 hours to produce the corresponding polyimides films.

2.2.5.3 The Synthesis of Polyimides via a One Step Process

Another method for the synthesis of polyimides is via a concerted polycondensation reaction between an appropriate dianhydride with different diamines in the presence of high boiling solvent such as m-cresol, α -chloronaphthalene, isoquinoline, nitrobenzene, o-dichlorobenzene or polar aprotic amide solvents and their mixtures.¹⁰⁸ The dianhydride and diamine monomers undergo polymerization at high temperature to provide the desired polyimides directly and the by-products are removed by an azeotropic distillation process. However, polymers with high molecular weight are seldom produced in the one step method due to deleterious side reactions.^{6, 7, 9, 117}

However, Jin and coworkers¹¹⁸ recently developed a one step process for the synthesis of polyimides. Completely cyclized polyimides were prepared in a homogeneous one-pot process in the presence of phosphorus pentoxide powder using polyphosphoric acid as solvent at 220 °C for 4 hours. Polyphosphoric acid has excellent solvating power and low volatility to produce polyimides with high molecular weights and higher thermal stability:



Polyimides can also be prepared via a one step process by the direct polycondensation of tetracarboxylic dianhydrides with aromatic diisocyanates. Marek and coworkers¹¹⁹ reported that the polycondensation reaction proceeds in a polar aprotic solvent such as N-methyl-2-pyrrolidone (NMP) at temperatures between 70 - 90 °C with the evolution of carbon dioxide:



Another route for the synthesis of polyimides via the one step process involves the use of dithioanhydrides and diamines as monomers. Oishi and coworkers¹²⁰ reported that the polycondensation reaction takes place in dimethylacetamide or pyridine at 100 - 140 °C with evolution of hydrogen sulfide to afford the resultant polyimides:



Polyimides have also been prepared by polycondensation of salt monomers based on 4,4'-oxydiphthalic acid and aliphatic diamines at 140 - 330 °C under high pressure 250 - 600 mpa.¹²¹



2.2.6 The Preparation of Sulfonated Polyimides

In general, sulfonated polyimides are prepared by the incorporation of sulfonic acid groups onto polymers backbone by two methods:

(a) The preparation of sulfonated polyimides by direct copolymerization reactions of sulfonated monomers with appropriate monomers. (b) The synthesis of sulfonated polyimides by post-polymerization sulfonation reactions which involves sulfonation reactions with the polyamic acid intermediate as well as the final polyimide derivative.

2.2.6.1 Sulfonated Polyimides by Direct Copolymerization of Sulfonated Monomers

The most efficient method for the preparation of sulfonated polyimides involves the direct step-growth copolymerization process using appropriate sulfonated monomers as substrates. Many synthetic routes have been developed for the synthesis of sulfonated diamines monomers.^{7, 10} For the preparation of sulfonated polyimides, a plethora of sulfonated diamine derivatives, which are commercially available, can be employed as precursors in the direct step-growth copolymerization with a specific dianhydride derivative. The following sulfonated diamines are extensively used as substrates for the synthesis of polyimides: 2,5-diaminobenzenesulfonic acid (DAB), 4,4'-diamino-2,2'-biphenyl disulfonic acid (BDA), 4,4'-diamino-5,5'-dimethyl disulfonic acid (6TS), 3,3'-disulfonate- bis[4-(3-aminophenoxy)phenyl]sulfone (SA-DADPS), 3-sulfo-4,4'bis(3-aminophenoxy)triphenyl phosphine oxide sodium salt (SBAPPO), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane disulfonic acid (BAHFDS), 4,4'- diaminodiphenylether-2,2'-disulfonic acid and 9,9'-bis(4,-aminophenyl)fluorine-2,7- disulfonic acid (BAPFDS):



Sulfonated diamines can be prepared by the reaction of the specific diamines or their nitro analogues with sulfonating agents via electrophilic aromatic substitution reactions. In aromatic diamines, the nature of sulfonation reactant determines the position of the sulfonic acid groups in the final product. For example, Fang and coworkers¹²² prepared different sulfonated diamines from the corresponding diamine precursors by the reaction with fuming sulfuric acid as sulfonating reagent to introduce the sulfonic acid group into the ortho position.



Sulfonated diamine derivatives can also be prepared by aromatic nucleophilic substutition methods.¹²³ For example, SA-DADPS was prepared from the reaction of the sodium salt of *m*-aminophenol with disodium -3,3´-disulfate-4,4´-dichlorodiphenylsulfone (S-DCDPS) as outlined by McGrath and coworkers:¹²⁴



The choice of the diamine precursor is essential for the design of a specific polymer with welldefined properties. The presence of flexible diamines increases the solubility and hydrolytic stability of the resultant polymer. Bulky diamines increase interchain space within the resultant polymers, leading to higher conductivity at high humidity and good hydrolytic properties.¹²² Disulfonated polyimides were prepared by the polymerization reactions of 1,4,5,8-naphthalene tetracarboxylic dianhydride (NDA) with the novel diamine SA-DADPS and bis[4-(3-aminophenoxy)phenyl]sulfone (*m*-BAPS) in a one-pot high temperature polycondensation reaction. By varying the molar ratio of the sulfonated diamine and unsulfonated diamine, sulfonated polyimide derivatives with 30 to 80 % sulfonation were obtained:¹²⁴



Chhabra and Choudhary¹²⁵ prepared a series of sulfonated polyimide copolymers from the polymerization reaction of 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) with 4,4⁻-diaminodiphenylether-2,2⁻-disulfonic acid (ODADS) and bis[4-(4-

aminophenoxy)phenylhexafluoropropane] (BDAF) using different molar ratios of monomers. The sulfonated polyimides displayed excellent thermal properties with the proton conductivity of the sulfonated polymers increasing with the degree of sulfonation:



2.2.6.2 Sulfonated Polyimides by Post-Polymerization Sulfonation Reactions

2.2.6.2.1 Sulfonated Polyimides by Post-Polymerization Sulfonation Methods: Direct Sulfonation of Polyamic Acid Intermediates

Sulfonated polyimides can be prepared by (a) the formation of the polyamic acid intermediate followed by (b) sulfonation of the polyamic acid prior to the imidization process.¹²⁶ For example, Deligoz and coworkers,¹²⁶ described a method whereby sulfonated polyimides were prepared by the sulfonation of the intermediate polyamic acid. The intermediate polyamic acid is formed by the reaction of benzophenone tetracarboxylic dianhydride (BTDA) with different diamine derivatives. The first step involves the sulfonation of the polyamic acid intermediate with concentrated sulfuric acid (95 - 98 %) at room temperature to afford the corresponding sulfonated polyamic acid. In the second step, the sulfonated polyamic acid was converted to the corresponding sulfonated polyimide polyimide by a thermal imidization process:



2.2.6.2.2 Sulfonated Polyimides by Post-Polymerization Sulfonation Methods: Direct Sulfonation of Polyimide Derivatives

In general, due to the low solubility of polyimides in most organic solvents, the postpolymerization sulfonation reactions of polyimides are not common in polymer synthesis since it is difficult to control the positions and amounts of sulfonic acid groups along the polymer backbone. Nevertheless, Marestin and coworkers¹²⁷ described the preparation of sulfonated polyimides using chlorosulfonic acid and sulfur trioxide/triethyl phosphate as sulfonating agents. Furthermore, Irvin and coworkers¹²⁸ outlined the synthesis of a series of polyimides via a two step process by the treatment of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and/or 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) with four different diamines followed by thermal imidization of the intermediate polyamic acid to form the resultant polyimide. The sulfonic acid groups were incorporated onto the polyimides backbone by subsequent sulfonation reactions of the polyimide precursor with sulfuric acid:



The present research work describes the syntheses of well-defined polyimide derivatives with the regiospecific introduction of the 1,1-diphenylethylene unit along the polyimide backbone. A series of new polyimides were prepared by polycondensation reactions of 4,4'- oxydiphthalic anhydride (7) with different mole percentage ratios of 2,2-bis[4-(4- aminophenoxy)phenyl]propane (8) and 1,1-bis(4-aminophenyl)ethylene (9) by a two step polyimide synthesis process to produce polyamic acid intermediates in the first step, followed by the formation of the corresponding polyimides via a thermal imidization process. Subsequent treatment of the appropriate polyimide derivative with sodium 3-mercapto-1-

propane sulfonate and AIBN via the thiol-ene reaction outlines a new method for the synthesis of new sulfonated polyimide derivatives with excellent chemical and thermal properties.

2.3 The Use of Functionalized 1,1-Diphenylethylene in Step-Growth Polymerization Methods

In general, functionalized 1,1-diphenylethylene derivatives are used in anionic polymerization methods for the synthesis of chain end functionalized polymers.¹²⁹ The reaction of simple organolithium compounds with 1,1-diphenylethylene derivatives affords the 1,1diphenylalkyllithium species in quantitative yields. Similarly, poly(styryl)lithium and poly(dienyl)lithium reacts with 1,1-diphenylethylene derivatives by addition reactions to produce polymeric compounds with the quantitative and regiospecific introduction of the 1,1diphenylethylene groups at the end of the polymer chain.¹³⁰ Futhermore, the use of 1,1diphenyethylene derivatives in anionic polymerization include: (a) the copolymerization of 1,1-diphenylethylene derivatives with styrenes and dienes; (b) the use of 1,1diphenylalkyllithium as initiator for anionic polymerization of alkyl methacrylates, styrenes and dienes; (c) the use of polymeric 1,1-diphenylalkyllithium as initiator for block copolymerization with dienes and styrene and (d) the reaction of polymeric organolithium compound with functionalized 1,1-diphenylethylene derivatives to form chain endfunctionalized polymers.¹³⁰ In addition, Summers and coworkers⁵⁸ described the preparation of dipyridyl functionalized poly(ether ether sulfone) derivatives by the reaction of lithiated poly(ether ether sulfone) with 2,2-vinylidenedipyridine to introduce the dipyridyl derivative pendant to the polymer chain:

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Limited reports on the introduction of the 1,1-diphenyethylene units along the polymer backbone engineering polymers have been reported in the literature.³³ Poly(ether ether sulfone), poly(ether ether ketone) and polyimides are engineering polymers with excellent chemical, thermal and mechanical properties. To extend its use in engineering applications, polymer functionalization reactions using 1,1-diphenylethylene derivatives have been

developed in order to improve polymer properties for specific applications. For example, Gao and Hay³³ prepared poly(ether ether sulfone) based on the 1,1-diphenylethylene unit by stepgrowth polymerization and induced post-polymerization crosslinking reactions to improve the thermal characteristics of the specific polymer system.



Jian and coworkers¹³¹ prepared photo-crosslinkable fluorinated poly(phthalazinone ether)s containing 1,1-diphenylethylene segments in the polymer backbone from a polycondensation reaction of decafluorobiphenyl with different mole percentage ratios of 4-(4-hydroxylphenyl)(2H)-phthalizin-1-one (DHPZ), 4,4-(hexafluoroisopropylidene)diphenol and 1,1-bis(4-hydroxyphenyl)ethylene (BHPE). The resultant polymers undergo crosslinking reactions under UV irradiation to afford polymers with improved chemical stability, high thermal stability and high glass transition temperature for applications such as passive optical waveguide devices:



In the present research work, well-defined poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives were prepared by step-growth polymerization methods according to the following procedure:

- (a) The novel synthesis of a series of disubstituted 1,1-diphenylethylene derivatives.
- (b) The utilization of the appropriate disubstituted 1,1-diphenylethylene derivative as a monomer in the preparation of a series of new poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives.

Due to the regiospecific introduction of the 1,1-diphenylethylene unit along the polymer backbone, post-polymerization functionalization reactions with the 1,1-diphenylethylene unit can be effected to improve the chemical and physical properties of the 1,1-diphenylethylene based engineering polymers.

2.4 Thiol-ene Chemistry

The hydrothiolation or the thiol-ene addition reaction is the addition reaction of electron deficient carbon-carbon double bonds with thiols. The addition reaction of olefins with thiols can be catalyzed by protic or Lewis acids or by free radical methods.^{60, 63-73} In general, the thiol-ene addition reaction proceeds via two methods:^{60, 63-73}

- (a) The radical addition of thiols to olefins via catalytic processes mediated by nucleophiles, acids, bases in the presence of highly polar solvent (DMF and water) in absence of catalyst.
- (b) Supramolecular catalysis using β-cyclodextrin.

Activated and non-activated alkenes as well as multiple-substituted alkenes have been employed in the thiol-ene reaction.^{60, 63-73} However, the reactivity of the alkene varies depending on reaction mechanism and substituents of the alkene. A variety of thiol derivatives, including functionalized thiol compounds, have been used as substrates in hydrothiolation reactions with alkenes. The reactivity of the specific thiol derivative depends on the S-H bond strength and the mechanism of the hydrothiolation reaction.^{60, 63-73}

The most efficient thiol-ene reaction is the radical hydrothiolation of olefins in the presence of 2,2'-azobis(isobutyronitrile) (AIBN) and involves the following steps:¹⁵

- (a) The thermal decomposition of the initiator, AIBN.
- (b) The formation of thiyl radical by reaction of the radical from the initiator, AIBN with the thiol.
- (c) The addition of the thiyl radical to the olefin group to form a carbon radical.

(d) The chain transfer reaction between the carbon radical and the thiol derivative to generate a new thiyl radical.



Guan and coworkers,¹⁵ reported the preparation of sulfonated poly(ether ether ketone)s via the thiol-ene method. Poly(ether ether ketone)s bearing unsatured propenyl group were prepared by step-growth copolymerization of 4,4'-difluorobenzophenone with 3,3'-diallyl-4,4'- dihydroxy biphenyl and 9,9'-bis(4-hydroxyphenyl)fluorene and to afford an intermediate poly(ether ether ketone) derivative with pendant propenyl groups. Sulfonation of the parent propenyl substituted copolymer with sodium 3-mercapto-1-propane sulfonate via thiol-ene chemistry produce the corresponding sulfonated poly(ether ether ketone) derivative.¹⁵



The current research work focuses on the regiospecific introduction of the 1,1diphenylethylene unit along the polymer backbone of poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives to produce a series of new polymer material which can be used as polymer precursors for sulfonation reactions via the hydrothiolation reaction. The presence of the 1,1-diphenylethylene unit within the polymer backbone of the new poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives acts as a synthon for subsequent thiol-ene reactions with sodium 3-mercapto-1-propane sulfonate in order to prepare new sulfonated engineering polymers for potential fuel cell technology applications.

CHAPTER 3

EXPERIMENTAL

3.1 Chemicals and Solvents

All chemicals and solvents were purchased from the Sigma Aldrich Chemical Company, unless otherwise stated. 4,4'-Dihydroxybenzophenone (97 %), *t*-butyldimethylsilyl chloride (97 %), imidazole (Saarchem Chemical Company), methyl lithium (1.6 M solution in diethyl ether), methyltriphenylphosphonium bromide, 4,4'-diaminobenzophenone (97 %), tetrabutylammonium fluoride (1 M solution in tetrahydrofuran), sodium 3-mercapto-1-propane sulfonate, 2,2'-azobis(isobutyronitrile) (Eastman Chemical Company), cesium fluoride (99 %), sodium hydrogen carbonate, anhydrous sodium sulfate, anhydrous potassium carbonate, N,N-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), hexane, petroleum ether, ethyl acetate, toluene, methanol, ethanol, acetone, dichloromethane and distilled water were used as received. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone before use. N,N-Dimethylformamide (DMF) was dried over molecular sieves before use.

3.2 Characterization

3.2.1 Size Exclusion Chromatography (SEC)

The determination of the molecular weights and molecular weight distributions of polymers were performed by size exclusion chromatography on a Waters Alliance Size Exclusion Chromatograph equipped with a Waters Alliance SEC autosampler and a Phenogel column (5 μ , 500 Å pore size, 1 K – 5 K MW range, 300×7.8 mm) in series with a refractive index detector and a dual angle laser light scattering detector. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL/min at 30 °C. For the SEC analyses of sulfonated polymers, a mixture of tetrahydrofuran and LiBr (2 g/L) was used as eluent.¹³² The SEC system and the Precision dual angle laser light scattering detector were calibrated with polystyrene standards (dn/dc = 0.186). The chromatograms were analyzed using the Varian Star Discovery 5.5 software package.

3.2.2 Nuclear Magnetic Resonance Spectrometry (NMR)

¹H NMR and ¹³C NMR spectra were recorded on a Varian Gemini 300 mHz and 75 mHz NMR spectrometer at ambient temperature. Deuterated chloroform (CDCl₃) or deuterated dimethylsulfoxide (DMSO-d₆) was used as solvent. In general, a 10 mg sample was dissolved in the appropriate solvent prior to the NMR analysis. The chemical shifts for the ¹H NMR and ¹³C NMR are reported in ppm relative to the CDCl₃ resonance at δ = 7.26 ppm and 77.36 ppm, respectively. In DMSO-d₆, the ¹H NMR and ¹³C NMR signals were reported in ppm relative to $\delta = 2.54$ ppm and 40.45 ppm, respectively.¹³³

3.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were recorded on a Digilab FTS-7000 spectrometer equipped with infra-red hyperspectral imaging and microscopy capabilities in the range from 4000 to 600 cm⁻¹. A solid sample was placed on a germanium crystal and maximum pressure was applied using the slip-clutch mechanism followed by the acquisition of the FTIR spectrum.

3.2.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analyses of different polymer samples were performed on a TA Instruments Hi-Res Q500 Thermogravimetric Analyser. In general, a 10 mg polymer sample was heated between 25 °C to 800 °C at a rate of 10 °C/min under nitrogen gas, where applicable.

3.2.5 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry of each polymer sample was performed on a TA Instruments Q100 research grade DSC equipped with a 50-position autosampler. Solid polymer samples of different masses between 5 - 10 mg were heated between 25 °C to 400 °C at a rate of 10 °C/min under nitrogen gas.

3.2.6 Thin Layer Chromatography (TLC)

TLC analyses of samples were carried out on silica gel plates (Silica Gel 60 F254) using specific organic solvents or mixtures of organic solvents as mobile phases.

3.2.7 Melting Point Determination

The melting points of samples are uncorrected and were determined on a Stuart SMP3 melting point apparatus.

3.2.8 X-Ray Diffraction (XRD)

X-ray diffraction analyses of the polymer samples in the powder form were performed at the CSIR, Pretoria on a PANalytical X'PertPRO materials research diffractometer using CuK α sealed tube X-ray source (wavelength 1.514 Å).

3.2.9 Atomic Force Microscopy (AFM)

Atomic Force Microscopy images of polymers were obtained at the CSIR, Pretoria with a Digital Instruments Nanoscope, Veeco, MMAFMLN-AM (Multimode) instrument. The poly(ether ether sulfone) and poly(ether ether ketone) samples were dissolved in NMP, spin coated onto glass and dried in an oven at 50 °C for 1 hour before AFM analyses. The polyimide samples in the film form with maximum sample size of 1 cm x 1 cm and maximum

sample height of 3 mm were prepared for AFM analyses. The AFM images were analyzed using the AFM imaging programs to determine the pores sizes and roughness of the membrane. The measurement of the distance variations in the surface of the polymer sample by two pairs of cursors is depicted in the following image:



3.2.10 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy analysis of polymers was performed at the University of Pretoria, Pretoria on a JEOL-Jem 2100 transmission electron microscope using an accelerating voltage of 200 kV. Each polymer sample was dispersed in ethanol and a drop of the heterogenous solution of the polymer was deposited onto a copper grid. The wet copper grids were allowed to dry on a filter paper at room temperature for 15 minutes prior the TEM analysis.

Cross-sectional TEM analyses were performed on polyimide and sulfonated polyimide samples in the film form. The membranes were embedded in epoxy resins and cured at 60 °C for 39 hours. The embedded samples were then cut in ultrathin sections at room temperature and placed onto copper grids prior to TEM analysis.

3.2.11 Elemental Analysis

Elemental analyses of polymers were performed at the University of Johannesburg on a FlashEA 4000 machine equipped with Eager Xperience software.

3.2.12 Energy Dispersive Spectroscopy (EDS)

Energy Dispersive Spectroscopy (EDS) was performed at the CSIR, Pretoria on a JEOL-JSM 7500F Scanning Electron Microscope to determine the elemental composition of the dense membranes of the different polymer samples.

3.2.13 Ion Exchange Capacity (IEC)

The IEC of the sulfonated polymers was calculated using the following equation:^{134, 135}

IEC = 1000 Sc/ MWs

- Where Sc : sulphur content (weight rate) determined by elemental analysis
 - MWs : the molecular weight of sulphur

IEC : in mmol/g

3.2.14 Dilute Solution Viscometry

The inherent viscosity¹³⁶ of polymers were measured using an Ubbelohde viscometer at 25 °C. Polymer samples with concentrations of 0.08 g/dL in concentrated sulfuric acid were prepared prior to dilute solution viscometry analysis.

3.3 Synthesis of Poly(ether ether sulfone)s based on Functionalized 1,1-Diphenylethylene Derivatives

3.3.1 Purification of 4,4'-Difluorodiphenylsulfone (1)

Commercially available 4,4[']-difluorodiphenylsulfone was purchased from the Sigma Aldrich Chemical Company and purified by recrystallization from ethanol to yield pure 4,4[']-difluorodiphenylsulfone (**1**) as a white crystalline solid, mp = 98 - 99 °C (Lit mp¹³⁷ = 98 - 99 °C).

3.3.2 Synthesis of 2,2-Bis(4-*t*-butyldimethylsiloxyphenyl)propane (2)

2,2-Bis(4-t-butyldimethylsiloxyphenyl)propane (2) was prepared according to the general procedure outlined by Quirk and Wang,¹³⁸ with modifications. Under an argon atmosphere, bisphenol A (10 g, 0.0438 mol), t-butyldimethylsilyl chloride (12.76 g, 0.0846 mmol), imidazole (7.95 g, 0.0001168 mol) and DMF (30 mL) were added to a 250 mL dry round bottom flask equipped with a magnetic stirrer bar. The flask was heated at 40 °C for 3 hours, with stirring, until the formation a homogenous solution. The desired product was then extracted with hexane $(1 \times 120 \text{ mL})$ and washed with 5 % aqueous NaHCO₃ (100 mL). The hexane layer was dried over anhydrous MgSO₄. After solvent removal in vacuo, the residue was purified by SiO₂ column chromatography with petroleum ether and ethyl acetate (80/20 =v/v) as eluent. After removal of the solvent, the resultant clear viscous product solidified on standing to give a white solid. Recrystallization of the white solid from absolute ethanol gave 17.83 g (94 %) of pure 2,2-bis(4-t-butyldimethylsiloxyphenyl)propane (2) as white crystals. TLC: R_f (petroleum ether/ethyl acetate = 80/20, v/v) = 0.9; mp = 69 - 72 °C; ¹H NMR (300 mHz, CDCl₃, δ , ppm) : $\delta = 0.21$ (s, 12H, 2 × Si-(CH₃)₂), 0.99 (s, 18H, 2 × Si-C-(CH₃)₃), 1.63 (s, 6H, $2 \times -CH_3$), 6.72 - 7.10 ppm (d × d, 8H, aromatic H); ¹³C NMR (75 mHz, CDCl₃ δ , ppm): $\delta = -4.40$ (Si-(<u>CH</u>₃)₂), 18.16 (<u>C</u>(CH₃)₃), 25.69 (C(<u>CH</u>₃)₃), 31.10 (<u>C</u>(CH₃)₂), 41.72 (C(<u>C</u>H₃)₂), 119.17, 127.66, 143.67 and 153.25 ppm (C-<u>C</u>, aromatics); FTIR (solid): 1259 cm⁻¹ (Si-CH₃).

3.3.3 Synthesis of 1,1-Bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3)

4,4'-Bis(*t*-butyldimethylsiloxy)benzophenone:

4,4'-Bis(t-buyldimethylsiloxy)benzophenone was prepared according to the method outlined by Quirk and Wang.¹³⁸ Under an argon atmosphere, 4,4⁻-dihydroxybenzophenone (11.70 g, 0.054 mol), t-butyldimethylsilyl chloride (15.91 g, 0.105 mol), imidazole (9.91 g, 0.145 mol) and N,N-dimethylformamide (30 mL) were added to a dry 250 mL round bottom flask equipped with a magnetic stirrer bar. The flask was heated at 40 $^{\circ}$ C with stirring, until the formation of a homogenous solution. After 3 hours, the desired product was extracted with hexane $(1 \times 120 \text{ mL})$ and washed with 5 % aqueous NaHCO₃ (100 mL). The hexane layer was dried over anhydrous MgSO₄. The solvent was removed using a rotary evaporator to give a white residue. The product was purified by SiO₂ column chromatography with toluene as eluent. After removal of toluene in vacuo, the product 4,4'-bis(tbutyldimethylsiloxy)benzophenone was isolated as a white solid. Recrystallization of the white solid from absolute ethanol gave 15.9 g (66 %) of pure 4,4'-bis (t-butyldimethylsiloxy)benzophenone as white crystals: TLC: R_f (toluene) = 0.6; mp: 52.5 - 55.7 °C; ¹H NMR $(300 \text{ mHz}, \text{CDCl}_3, \delta, \text{ppm}): \delta = 0.24 \text{ (s, 12H, } 2 \times \text{Si-(CH}_3)_2\text{), } 0.99 \text{ (s, 18H, } 2 \times \text{Si-C-(CH}_3)_3\text{)}$ and 6.88 - 7.74 ppm (d × d, 8H, aromatic H); 13 C NMR (75 mHz, CDCl₃, δ , ppm) : δ = -4.40 (Si-(<u>CH</u>₃)₂), 18.19 (C(<u>C</u>H₃)₃), 25.56 (<u>C</u>(CH₃)₃), 119.56, 131.21, 132.10, 159.44 (C-<u>C</u>, aromatics) and 194.60 ppm (C=O). FTIR (solid): 1272 cm⁻¹ (vs, Si-CH₃) and 1695 cm⁻¹ (s, C=O).

1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3):

1,1-Bis[4-(t-butyldimethylsiloxy)phenyl]ethylene (3) was prepared according to the procedure outlined by Quirk and Wang,¹³⁸ with modifications. Under a nitrogen atmosphere, methyllithium (26.60 mL of a 1.6 M solution in diethyl ether, 0.0425 mol) was added to methyltriphenylphosphonium bromide (13 g, 0.034 mol) in dry THF (50 mL) at room temperature. The reaction mixture was stirred at room temperature for 2 hours to ensure complete ylide formation. A solution of 4,4'-bis(t-butyldimethylsiloxy)benzophenone (15 g, 0.034 mol) in dry THF (50 mL) was added to the ylide solution at 0 °C and the resultant reaction mixture was stirred at room temperature for 12 hours. The reaction was terminated by the addition of methanol (2 mL). The triphenylphosphine oxide, which precipitated from the reaction, was removed by filtration. After removal of the solvent from the filtrate using a rotary evaporator, the clear viscous residue was extracted with petroleum ether (120 mL). After removal of petroleum ether in vacuo, the crude product was isolated as viscous product which solidified on standing to give a white solid. Recrystallization of the white product from absolute ethanol gave 9.6 g (63 %) of pure 1,1-bis[4-(t-butyldimethylsiloxy)phenyl]ethylene (3) as fine, white crystals: mp = 55.9 - 56.4 °C (Lit mp¹³⁸ = 56 - 57.5 °C); TLC: R_f (toluene) = 0.9; ¹H NMR (300 mHz, CDCl₃, δ , ppm): $\delta = 0.21$ (s, 12H, 2 × Si-(CH₃)₂), 0.99 (s, 18H, 2 × Si-C-(C<u>H</u>₃)₃), 5.28 (s, 2H, C=C<u>H</u>₂) and 6.77 - 7.20 ppm (d × d, 8H, aromatic H). ¹³C NMR $(75 \text{ mHz}, \text{CDCl}_3, \delta, \text{ppm}): \delta = -4.38 \text{ (Si-}(\underline{\text{CH}}_3)_2), 18.21 \text{ (C}(\underline{\text{CH}}_3)_3), 25.69 \text{ (C}(\text{CH}_3)_3), 111.66$ (C=<u>C</u>H₂), 134.81 (<u>C</u>=CH₂), 119.57, 129.361, 149.17 and 155.39 ppm (C-<u>C</u>, aromatics); FTIR (solid): 1265 cm⁻¹ (vs, Si-CH₃) and 889 cm⁻¹ (m, C=CH₂).

3.3.4 Purification of Bisphenol A (4)

Bisphenol A (4) was purchased from the Sigma Aldrich Chemical Company and purified by recrystallization from toluene to afford pure bisphenol A (4) as white crystals; mp = 156 - 158 °C (Lit $mp^{139} = 156 - 158$ °C).

3.3.5 Synthesis of 1,1-Bis(4-hydroxyphenyl)ethylene (5)

A new method for the preparation of 1,1-bis(4-hydroxyphenyl)ethylene (5) was developed by the treatment of 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3) with tetrabutylammonium fluoride using the general functional group transformation procedure described by De Meulenaer and coworkers.¹⁴⁰ Under an argon atmosphere, 1,1-bis[4-(*t*butyldimethylsiloxy)phenyl]ethylene (3) (7.06 g, 0.01604 mol) was added to dry THF (10 mL) in a dry 100 mL round bottom flask equipped with a magnetic stirrer bar. Tetrabutylammonium fluoride (32 mL of a 1 M solution in THF, 0.03209 mol) was then added to the clear solution and the resultant mixture was stirred at room temperature. After 2 hours, the reaction was quenched with water (10 mL). The crude product was extracted with diethyl ether $(3 \times 15 \text{ mL})$ and the ether layer was dried over anhydrous Na₂SO₄. After removal of the solvent in vacuo, the crude product was obtained as a pale yellow solid. Recrystallization of the crude product from ethanol/water (1/18 = v/v) gave 2 g (62 %) of pure 1,1-bis(4hydroxyphenyl)ethylene (5) as fine yellow crystals: TLC: R_f (toluene) = 0; mp: 151.1 - 152.8 °C (Lit mp¹⁴¹ = 150 – 152 °C); ¹H NMR (300 mHz, DMSO-d₆ δ , ppm): δ = 5.17 (s, 2H, C=CH₂), 6.71 - 7.21 (d × d, 8H, aromatic H), 9.50 ppm (s, 2H, 2× OH); ¹³C NMR (75 mHz,

DMSO, δ , ppm): δ = 110.71 (C=<u>C</u>H₂), 132.44 (<u>C</u>=CH₂), 115.47, 129.56, 140.31 and 157.69 ppm (C-<u>C</u>, aromatics); FTIR (solid): 3240 cm⁻¹ (vs, OH) and 892 cm⁻¹ (m, C=CH₂).

3.3.6 Synthesis of Poly(ether ether sulfone)s by Step-Growth Polymerization Methods

3.3.6.1 The Cesium Fluoride Catalyzed Polymerization of Dihalogenated Diaryl Sulfones with Silylated Bisphenols

A series of new poly(ether ether sulfone) derivatives (**PSU-1** to **PSU-5**) was prepared by the catalytic arylation polymerization reactions of dihalogenated diaryl sulfones with silylated bisphenols as outlined by Kricheldorf and coworkers.^{29, 30} In a typical procedure, poly(ether ether sulfone) **PSU-2** was prepared as follows: Under an argon atmosphere, 4,4'-difluorodiphenylsulfone (**1**) (1.47 g, 0.00581 mol), 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) (2.03 g, 0.00469 mol), 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) (0.49 g, 0.00112 mol), cesium fluoride (30 mg) and NMP (6 mL) were added in a 100 mL round bottom flask equipped with a magnetic stirrer bar. The reaction mixture was heated to 150 °C for 12 hours, with rapid stirring. The reaction flask was then cooled to room temperature and diluted with dichloromethane (4 mL). The polymer product was precipitated into methanol, filtered and vacuum dried at 80 °C to give **4.1** g of poly(ether ether sulfone) **PSU-2** as a white solid: SEC: $\overline{M}_n = 9.6 \times 10^3$ g/mol and

 $M_w/M_n = 1.23$; ¹H NMR (300 mHz, CDCl₃, δ , ppm): $\delta = 1.68$ (s, 6H, -C-(C<u>H</u>₃)₂); 5.44 (s, 2H,

C=C<u>H</u>₂); 6.91 - 7.88 ppm (m, 32H, aromatic H); ¹³C NMR (75 mHz, CDCl₃, δ , ppm): δ =

30.93 (C-(<u>C</u>H₃)₂), 42.39 (<u>C</u>-(CH₃)₂), 114.62 (C=<u>C</u>H₂), 135.27 (<u>C</u>=CH₂), 117.64, 117.90, 119.69, 119.80, 119.94, 127.84, 128.42, 129.67, 129.74, 129.82, 129.95, 130.16, 130.28, 135.27, 135.35, 135.71, 135.98, 147.15, 147.25, 148.00, 152.79, 161.63, 161.95, 162.00 ppm (C-<u>C</u>, aromatics); FTIR (solid): 1487 and 1584 cm⁻¹ (vs, C=C aromatic) and 1149 cm⁻¹ (vs, SO₂).

Experimental data for the preparation of the different poly(ether ether sulfone) derivatives are outlined in the following table:

Polymer	Monomer (1)	Monomer (2)	Monomer (3)	CsF
PSU-1	0.5 g	0.84 g	-	30 mg
	0.00196 mol	0.00196 mol		
PSU-2	1.47 g	2.03 g	0.49 g	30 mg
	0.00581 mol	0.00469 mol	0.00112 mol	
PSU-3	1.02 g	0.18 g	0.88 g	30 mg
	0.00401 mol	0.002 mol	0.002 mol	
PSU-4	0.73 g	0.26 g	1.09 g	30 mg
	0.00298 mol	0.00062 mol	0.00239 mol	
PSU-5	0.57 g	-	1 g	30 mg
	0.00227 mol		0.00227 mol	

3.3.6.2 The Potassium Carbonate Catalyzed Polymerization of Dihalogenated Diaryl Sulfones with Bisphenols

Different poly(ether ether sulfone) derivatives (**PSU-6** to **PSU-10**) were prepared according to the general procedure outlined by Gao and coworkers.³³ In a typical procedure, poly(ether ether sulfone) **PSU-7** was prepared as follows: Under an argon atmosphere, 4,4'difluorodiphenylsulfone (1) (0.4 g, 0.00157 mol), bisphenol A (4) (0.29 g, 0.00126 mol), 1,1bis(4-hydroxyphenyl)ethylene (5) (0.067 g, 0.000315 mol), anhydrous K_2CO_3 (0.405 g, 0.00293 mol), toluene (4 mL) and N,N-dimethylacetamide (8 mL) were added to a 100 mL round bottom flask equipped with a magnetic stirrer bar and a Dean-Stark apparatus. The reaction mixture was heated at 165 °C for 3 hours, with rapid stirring. The reaction flask was cooled to 100 °C and the viscous product diluted with cold N,N-dimethylacetamide (5 mL). The reaction mixture was filtered and the filtrate neutralized with acetic acid. The filtrate was coagulated into methanol. The polymer was isolated by filtration and washed with methanol and water. The polymer product was boiled in distilled water for 1 hour to remove any trapped salts, filtered and vacuum dried at 80 °C to afford 0.40 g of poly(ether ether sulfone) **PSU-7** as a white solid: SEC: $\overline{M}_n = 14.7 \times 10^3 \text{g/mol}, \overline{M}_w / \overline{M}_n = 1.23$; ¹H NMR (300 mHz, $CDCl_{3}$, δ , ppm): $\delta = 1.69$ (s, 6H, -C-(CH₃)₂); 5.45 (s, 2H, C=CH₂); 6.92 - 7.85 ppm (m, 32H, aromatic H); ¹³C NMR (75 mHz, CDCl₃, δ , ppm): δ = 30.90 (C-(<u>C</u>H₃)₂), 42.40 (<u>C</u>-(CH₃)₂), 114.62 (C=CH₂), 135.30 (C=CH₂), 114.82, 116.40, 116.72, 117.65, 117.90, 119.70, 119.81, 119.96, 127.85, 128.42, 129.68, 129.75, 129.83, 129.97, 130.20, 130.26, 135.29, 135.37, 135.76, 135.94, 147.17, 147.27, 148.05, 152.81, 161.65, 161.98, 162.00 ppm (C-C, aromatics); FTIR (solid): 1487 and 1584 cm⁻¹ (vs, C=C aromatic) and 1149 cm⁻¹ (vs, SO₂).

Experimental details for the preparation of a series of poly(ether ether sulfone) derivatives are outlined as follows:

Polymer	Monomer (1)	Monomer (4)	Monomer (5)	K ₂ CO ₃
PSU-6	0.5 g	0.45 g	-	0.507 g
	0.00196 mol	0.00196 mol		0.00366 mmol
PSU-7	0.4 g	0.29 g	0.067 g	0.405 g
	0.00157 mol	0.00126 mol	0.00031 mol	0.00293 mol
PSU-8	0.4 g	0.18 g	0.17 g	0.405 g
	0.00157 mol	0.0007 mol	0.0007mmol	0.00293 mol
PSU-9	0.22 g	0.04 g	0.15 g	0.22 g
	0.0008 mol	0.00017 mol	0.00070 mol	0.00159 mol
PSU-10	0.167 g	-	0.14 g	0.17 g
	0.00066 mol		0.00066 mol	0.00123 mol

3.3.7 Preparation of Sulfonated Poly(ether ether sulfone)s

Sulfonated poly(ether ether sulfone) was prepared by the general procedure for the thiol-ene reaction as outlined by Guan and coworkers.¹⁵ Under a nitrogen atmosphere, poly(ether ether sulfone) **PSU-2** (1 g, 0.469 mmol, $\overline{M}_n = 9.6 \times 10^3$ g/mol and $\overline{M}_w/\overline{M}_n = 1.23$), sodium 3-mercapto-1-propane sulfonate (0.16 g, 0.938 mmol) and 2,2´-azobis(isobutyronitrile) (0.04 g, 0.281 mmol) were added to a 250 mL round bottom flask equipped with a magnetic stirrer bar, followed by the addition of 7.5 mL of a mixed solvent system of NMP and DMSO (2/1, v/v).

The reaction mixture was heated at 75 °C for 5 days, with stirring. The reaction mixture was then precipitated into water to give a white solid. Further purification of the white polymer product by dialysis with 30 % aqueous acetone for 3 days gave 0.89 g of sulfonated poly(ether ether sulfone) **SPSU-2** as a white solid: SEC: $\overline{M}_n = 10.8 \times 10^3$ g/mol, $\overline{M}_w/\overline{M}_n = 1.20$; ¹H NMR (300 mHz, DMSO-d₆, δ , ppm): $\delta = 1.62$ (s, 6H, -C-(CH₃)₂), 1.87 – 1.92 (quin, 2H, CH₂-CH₂-CH₂), 2.15 - 2.17 (t, 2H, (CH₂)₂-CH₂-S), 2.66 – 2.74 (t, (CH₂)₂-CH₂-SO₃Na), 4.35 – 4.39 (t, 1H, R₂-CH-CH₂-S), 4.44 – 4.46 (d, 2 H, R₂-CH-CH₂-S), 6.68 – 8.00 ppm (m, 20H, aromatic H); ¹³C NMR (75 mHz, DMSO-d₆, δ , ppm): $\delta = 25.91$ (CH₂-CH₂-CH₂-SO₃Na), 30.64 ((CH₂)₂-CH₂-S), 31 (C-(CH₃)₂), 42.43 (C-(CH₃)₂), 63.59 (R₂-CH-CH₂-S-CH₂), 115.24, 135.60, 118.28, 120.26, 120.67, 128.93, 130.2, 147.32, 152.79, 161.91 ppm (C-C, aromatics); FTIR (solid): 1488 and 1585 cm⁻¹ (vs, C=C aromatic), 1151 cm⁻¹ (vs, SO₂) and 1027 cm⁻¹ (w, SO₃Na).

3.4 Synthesis of Poly(ether ether ketone)s based on Functionalized1,1-Diphenylethylene Derivatives

3.4.1 Purification of 4,4'-Difluorobenzophenone (6)

4,4´-Difluorobenzophenone (6) was purchased from the Sigma Aldrich Chemical Company and purified by recrystallization from ethanol to give pure 4,4´-difluorobenzophenone (6) as white crystals: mp = 102 - 104 °C (Lit mp^{137} : 102 - 104 °C).
3.4.2 Synthesis of 2,2-Bis(4-*t*-butyldimethylsiloxyphenyl)propane (2)

2,2-Bis(4-t-butyldimethylsiloxyphenyl)propane (2) was prepared according to the general procedure outlined by Quirk and Wang,¹³⁸ with modifications. Under an argon atmosphere, bisphenol A (10 g, 0.0438 mol), t-butyldimethylsilyl chloride (12.76 g, 0.0846 mmol), imidazole (7.95 g, 0.0001168 mol) and DMF (30 mL) were added to a 250 mL dry round bottom flask equipped with a magnetic stirrer bar. The flask was heated at 40 °C for 3 hours, with stirring, until the formation of a homogenous solution. The desired product was then extracted with hexane $(1 \times 120 \text{ mL})$ and washed with 5 % aqueous NaHCO₃ (100 mL). The hexane layer was dried over anhydrous MgSO₄. After solvent removal in vacuo, the residue was purified by SiO₂ column chromatography with petroleum ether and ethyl acetate (80/20 =v/v) as eluent. After removal of the solvent, the resultant clear viscous product solidified on standing to give a white solid. Recrystallization of the white solid from absolute ethanol gave 17.83 g (94 %) of pure 2,2-bis(4-t-butyldimethylsiloxyphenyl)propane (2) as white crystals. TLC: R_f (petroleum ether/ethyl acetate, 80/20, v/v) = 0.9; mp = 69 - 72 °C; ¹H NMR (300 mHz, CDCl₃, δ , ppm) : $\delta = 0.21$ (s, 12H, 2 × Si-(CH₃)₂), 0.99 (s, 18H, Si-C-(CH₃)₃), 1.63 (s, 6H, $2 \times -CH_3$), 6.72 - 7.10 ppm (d × d, 8H, aromatic H); ¹³C NMR (75 mHz, CDCl₃, δ , ppm): $\delta = -4.40 (\text{Si} - (\text{CH}_3)_2), 18.16 (\text{C}(\text{CH}_3)_3), 25.69 (\text{C}(\text{CH}_3)_3), 31.10 (\text{C}(\text{CH}_3)_2), 41.72 (\text{C}(\text{CH}_3)_2), 18.16 (\text{C}(\text{CH}_3)_3), 25.69 (\text{C}(\text{CH}_3)_3), 31.10 (\text{C}(\text{CH}_3)_2), 41.72 (\text{C}$ 119.17, 127.66, 143.67 and 153.25 ppm (C-C, aromatics); FTIR (solid): 1259 cm⁻¹ (Si-CH₃).

3.4.3 Synthesis of 1,1-Bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3)

4,4'-Bis(*t*-butyldimethylsiloxy)benzophenone:

4,4'-Bis(t-buyldimethylsiloxy)benzophenone was prepared according to the method outlined by Quirk and Wang.¹³⁸ Under an argon atmosphere, 4,4⁻-dihydroxybenzophenone (11.70 g, 0.054 mol), t-butyldimethylsilyl chloride (15.91 g, 0.105 mol), imidazole (9.91 g, 0.145 mol) and DMF (30 mL) were added to a dry 250 mL round bottom flask equipped with a magnetic stirrer bar. The flask was heated at 40 °C with stirring, until the formation of a homogenous solution. After 3 hours, the desired product was extracted once with hexane (1×120 mL) and washed with 5 % aqueous NaHCO₃ (100 mL). The hexane layer was dried over anhydrous MgSO₄. The solvent was removed using a rotary evaporator to give a white residue. The product was purified by SiO₂ column chromatography with toluene as eluent. After removal of toluene *in vacuo*, the crude product 4,4'-bis(t-butyldimethylsiloxy)benzophenone was isolated as a white solid. Recrystallization of the white solid from absolute ethanol gave 15.9 g (66 %) of pure 4,4'-bis (t-butyldimethylsiloxy)benzophenone as white crystals: TLC: R_f (toluene) = 0.6; mp: 52.5 - 55.7 °C; ¹H NMR (300 mHz, CDCl₃, δ , ppm): δ = 0.24 (s, 12H, 2 × Si-(CH₃)₂), 0.99 (s, 18H, 2 × Si-C-(CH₃)₃) and 6.88 - 7.74 ppm (d × d, 8H, aromatic H); 13 C NMR (75 mHz, CDCl₃, δ , ppm) : δ = -4.40 (Si-(<u>CH</u>₃)₂), 18.19 (C(<u>CH</u>₃)₃), 25.56 (<u>C</u>(CH₃)₃), 119.56, 131.21, 132.10, 159.44 (C-C, aromatics) and 194.60 ppm (C=O). FTIR (solid): 1272 cm⁻¹ (vs, Si-CH₃) and 1695 cm⁻¹ (s, C=O).

1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3):

1,1-Bis[4-(t-butyldimethylsiloxy)phenyl]ethylene (3) was prepared according to the procedure outlined by Quirk and Wang,¹³⁸ with modifications. Under a nitrogen atmosphere, methyllithium (26.60 mL of a 1.6 M solution in diethyl ether, 0.0425 mol) was added to methyltriphenylphosphonium bromide (13 g, 0.034 mol) in dry THF (50 mL) at room temperature. The reaction mixture was stirred at room temperature for 2 hours to ensure complete ylide formation. A solution of 4,4'-bis(t-butyldimethylsiloxy)benzophenone (15 g, 0.034 mol) in dry THF (50 mL) was added to the ylide solution at 0 °C and the resultant reaction mixture was stirred at room temperature for 12 hours. The reaction was terminated by the addition of methanol (2 mL). The triphenylphosphine oxide, which precipitated from the reaction, was removed by filtration. After removal of the solvent from the filtrate using a rotary evaporator, the clear viscous residue was extracted with petroleum ether (120 mL). After removal of petroleum ether in vacuo, the crude product was isolated as viscous product which solidified on standing to give a white solid. Recrystallization of the white product from absolute ethanol gave 9.6 g (63 %) of pure 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3) as fine, white crystals: mp = 55.9 - 56.4 °C (Lit mp¹³⁸ = 56 - 57.5 °C); TLC: R_f (toluene) = 0.9; ¹H NMR (300 mHz, CDCl₃, δ , ppm): $\delta = 0.21$ (s, 12H, 2 × Si-(CH₃)₂), 0.99 (s, 18H, 2 × Si-C-(C<u>H</u>₃)₃), 5.28 (s, 2H, C=C<u>H</u>₂) and 6.77 - 7.20 ppm (d × d, 8H, aromatic H); 13 C NMR $(75 \text{ mHz}, \text{CDCl}_3, \delta, \text{ppm}): \delta = -4.38 \text{ (Si-}(\underline{\text{CH}}_3)_2), 18.21 \text{ (C}(\underline{\text{CH}}_3)_3), 25.69 \text{ (C}(\text{CH}_3)_3), 111.66$ (C=<u>C</u>H₂), 134.81 (<u>C</u>=CH₂), 119.57, 129.361, 149.17 and 155.39 ppm (C-<u>C</u>, aromatics); FTIR (solid): 1265 cm⁻¹ (vs, Si-CH₃) and 889 cm⁻¹ (m, C=CH₂).

3.4.4 Synthesis of Poly(ether ether ketone)s by Step-Growth Polymerization

3.4.4.1 The Cesium Fluoride Catalyzed Polymerization of Dihalogenated Diaryl Ketones with Silylated Bisphenols

A series of poly (ether ether ketone) derivatives (**PEEK-1** to **PEEK-5**) was prepared by the catalytic arylation reaction of dihalogenated diaryl ketones with silylated bisphenols according to the procedures outlined by Kricheldorf.^{30, 142} In a typical procedure, poly(ether ether ketone) **PEEK-2** was prepared as follows: Under an argon atmosphere, 4,4′-

difluorobenzophenone (6) (1.238 g, 0.00566 mol), 2,2-bis(4-t-

butyldimethylsiloxyphenyl)propane (2) (1.96 g, 0.00452 mol), 1,1-bis[4-(t-

butyldimethylsiloxy)phenyl]ethylene (**3**) (0.5 g, 0.00112 mol), cesium fluoride (30 mg) and NMP (6 mL) were added in a 100 mL round bottom flask equipped with a magnetic stirrer bar. The reaction mixture was heated at 150 °C for 12 hours, with rapid stirring. The reaction flask was then cooled to room temperature and the reaction mixture diluted with dichloromethane (4 mL). The reaction mixture was then coagulated into excess methanol. The polymer product was filtered and vacuum dried at 80 °C to give 2.64 g of poly(ether ether ketone) **PEEK-2** as a white solid: SEC: $\overline{M}_n = 6.9 \times 10^3$ g/mol, $\overline{M}_w/\overline{M}_n = 1.20$; ¹H NMR (300 mHz, CDCl₃, δ , ppm): $\delta = 1.71$ (s, 6H, C-(C<u>H</u>₃)₂); 5.45 (s, 2H, C=C<u>H</u>₂); 6.98 - 7.81 ppm (m, 32H, aromatic H); ¹³C NMR (75 mHz, CDCl₃, δ , ppm): $\delta = 30.99$ (C-(CH₃)₂), 42.34 (C-(CH₃)₂), 114.81 (C=CH₂), 132.29 (C=CH₂), 117.11, 117.41, 119.53, 119.63, 127.87, 128.318, 129.86, 137.56, 146.72, 153.41, 161.10, 161.42 and 161.75 (C-C, aromatics), 194.28 ppm (C=O); FTIR (solid): 1654 cm⁻¹ (m, C=O) and 1497 and 1584 cm⁻¹ (vs, C=C aromatic). A series of poly(ether ether ketone) derivatives was prepared according to the reaction stoichiometry outlined in the following table.

Polymer	Monomer (6)	Monomer (2)	Monomer (3)	CsF
PEEK-1	0.5 g	1.049 g	-	30 mg
	0.00242 mol	0.00242 mol		
PEEK-2	1.234 g	1.96 g	0.5 g	30 mg
	0.00566 mol	0.00452 mol	0.00112 mol	
PEEK-3	0.86 g	0.90 g	0.87 g	30 mg
	0.00394 mol	0.00197 mol	0.00197 mol	
PEEK-4	0.64 g	0.25 g	1.018 g	30 mg
	0.00293 mol	0.00054 mol	0.00231 mol	
PEEK-5	0.5 g	-	1.068 g	30 mg
	0.00242 mol		0.00242 mol	

3.4.5 Preparation of Sulfonated Poly(ether ether ketone)s

Sulfonated poly(ether ether ketone) **SPEEK-2** was prepared by the procedure of the thiol-ene reaction as outlined by Guan and coworkers.¹⁵ Under a nitrogen atmosphere, poly(ether ether ketone) **PEEK-2** (1 g, 0.496 mmol, $\overline{M}_n = 6.9 \times 10^3$ g/mol, $\overline{M}_w/\overline{M}_n = 1.20$), sodium 3-mercapto-1-propane sulfonate (0.17 g, 0.992 mmol) and 2,2′-azobis(isobutyronitrile) (0.04 g, 0.297 mmol) were added to a 250 mL round bottom flask equipped with a magnetic stirrer bar, followed by the addition of 7.5 mL of a mixed solvent of NMP and DMSO (2:1, v/v).

The reaction mixture was heated at 75 °C for 5 days with stirring. The reaction mixture was then precipitated into water to afford a white solid. The polymer product was isolated by filtration and vacuum dried at 80 °C. Purification of the white polymer product by dialysis with 30 % aqueous acetone for 3 days gave 0.83 g of sulfonated poly(ether ether ketone) **SPEEK-2** as a white solid: SEC: $\overline{M}_n = 7.1 \times 10^3 \text{ g/mol}$, $\overline{M}_w / \overline{M}_n = 1.21$; ¹H NMR (300 mHz, CDCl₃, δ , ppm): $\delta = 1.65$ (s, 6H, -C-(C<u>H</u>₃)₂), 1.84 – 1.92 (quin, 2H, CH₂-C<u>H</u>₂-CH₂), 2.15 – 2.20 (t, 2H, (CH₂)₂-C<u>H</u>₂-S), 2.67 – 2.75 (t, (CH₂)₂-C<u>H</u>₂-SO₃Na), 4.37 – 4.41 (t, 1H, R₂-C<u>H</u>-CH₂-CH₂-S), 4.45 – 4.47 (d, 2H, R₂-CH-C<u>H</u>₂-S), 6.70 – 7.70 ppm (m, 20H, aromatic H); ¹³C NMR (75 mHz, DMSO-d₆, δ , ppm): $\delta = 30.59$ ((CH₂)₂-<u>C</u>H₂-S), 31.19 (C-(<u>C</u>H₃)₂), 42.40 (<u>C</u>-(CH₃)₂), 63.56 (<u>C</u>H-CH₂-S-CH₂), 115.21, 132.90, 115.94, 116.23, 117.54, 119.18, 119.99, 127.85, 128.84, 132.16, 132.62, 132.79, 146.968, 153.33, 161.31 (C-<u>C</u>, aromatics), 193.59 ppm (C=O); FTIR (solid): 1657 cm⁻¹ (m, C=O), 1496 and 1590 cm⁻¹ (vs, C=C aromatic) and 1024 cm⁻¹ (w, SO₃Na).

3.5 Synthesis of Polyimides based on Functionalized 1,1-Diphenylethylene Derivatives

3.5.1 Purification of 4,4'-Oxydiphthalic Anhydride (7)

Commercially available 4,4[']-oxydiphthalic anhydride (7) was purchased from Sigma Aldrich Chemical Company and purified by recrystallization from acetic anhydride to afford pure 4,4[']oxydiphthalic anhydride (7) as white crystals with a melting point of 224 - 226 °C (Lit mp^{143,} $^{144} = 224 - 226$ °C).

3.5.2 Purification of 2,2-Bis[4-(4-aminophenoxy)phenyl]propane (8)

2,2-Bis[4-(4-aminophenoxy)phenyl]propane (8) was purchased from the Sigma Aldrich Chemical Company (98 %) and dried in the oven at 60 °C for 12 hours to give 2,2-bis[4-(4aminophenoxy)phenyl]propane (8) as white solid: mp: 127 - 130 °C (Lit mp¹⁴⁵ = 127 - 130 °C).

3.5.3 Synthesis of 1,1-Bis(4-aminophenyl)ethylene (9)

The preparation of 1,1-bis(4-aminophenyl)ethylene (9) was effected by the general procedure outlined by Ndawuni.¹⁴⁶ Under a nitrogen atmosphere, methyllithium (15.63 mL of a 1.6 M solution in anhydrous diethyl ether, 0.025 mol) was added to methyltriphenylphosphonium bromide (8.93 g, 0.024 mol) in dry THF (100 mL) at room temperature. The reaction mixture was stirred at room temperature for 2 hours to ensure complete ylide formation. A solution of 4,4'-diaminobenzophenone (5.0 g, 0.0236 mol) in dry THF (100 mL) was added to the ylide solution at 0 °C and the resultant reaction mixture was heated to reflux for 12 hours. The reaction was terminated by the addition of cold methanol (1 mL). The triphenylphosphine oxide, which precipitated from solution, was removed by filtration. After removal of the filtrate solvent *in vacuo*, the crude product was purified by SiO₂ column chromatography using petroleum ether/ethyl acetate (50/50, v/v) as eluent. After removal of the solvent, the product was isolated as a yellow solid. Recrystallization of the crude product from ethanol/water (80/20, v/v) gave 2.58 g (52 %) of pure 1,1-bis(4-aminophenyl)ethylene (9) as yellow crystals: TLC: R_f (petroleum ether/ethyl acetate = 50/50, v/v) = 0.35; mp: 161.5 - 163.1 °C (Lit mp¹⁴⁷ =

170 – 172 °C); ¹H NMR (300 mHz, CDCl₃, δ , ppm): δ = 3.69 (bs, 2 H, -N<u>H</u>₂), 5.19 (s, 2 H, C=C<u>H</u>₂) and 6.61 - 7.25 ppm (d × d, 8H, aromatic H); ¹³C NMR (75 mHz, CDCl₃, δ , ppm): δ = 109.71 (C=<u>C</u>H₂), 132.31 (<u>C</u>=CH₂), 114.56, 129.35, 145.93 and 149.46 ppm (C-<u>C</u>, aromatics); FTIR (solid): 3435 cm⁻¹ (m, N-H) and 890 cm⁻¹ (m, C=CH₂).

3.5.4 The Synthesis of Polyimides by Step-Growth Polymerization

3.5.4.1 Polyimide Synthesis by the Two Step Thermal Imidization Process

A series of different polyimide derivatives, (**PI-1** to **PI-5**) was prepared by the general polyimide synthesis method by a two step thermal imidization process according to the procedure outlined by Li and coworkers.¹⁰⁹ In a typical procedure, polyimide **PI-2** was prepared according to the following process: Under a nitrogen atmosphere, 4,4'-oxydiphthalic anhydride (**7**) (0.5 g, 0.0003223 mol), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**8**) (0.529 g, 0.001289 mol) and 1,1-bis(4-aminophenyl)ethylene (**9**) (0.059 g, 0.0003223 mol) in N,N-dimethylacetamide (10 mL) were added to a dry 100 mL round bottom flask equipped with a magnetic stirrer bar. The reaction mixture was stirred at room temperature for 24 hours, with rapid stirring. The resultant polyamic acid was cast into a glass plate and subjected to a thermal imidization process at 100 °C, 200 °C and 250 °C for one hour each, respectively. After the thermal imidization process, the glass with the polymer film was cooled to 25 °C and placed into water to remove the film. The film was vacuum dried at 80 °C to give 1.48 g of polyimide **PI-2** as a brown film: η_{inh} : 0.24 dL/g at 25 °C; ¹H NMR (300 mHz, CDCl₃, δ , ppm): $\delta = 1.65$ (s, 6H, C-(C<u>H</u>₃)₂); 5.65 (s, 2H, C=C<u>H</u>₂); 6.99 - 8.10 ppm (m, 36H, aromatic H); ¹³C

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NMR (75 mHz, CDCl₃, δ , ppm): δ = 31.14 (C-(<u>C</u>H₃)₂), 42.28 (<u>C</u>-(CH₃)₂), 114.19 (C=<u>C</u>H₂), 134.98 (<u>C</u>=CH₂), 118.74, 119.02, 124.79, 125.98, 126.22, 127.31, 127.94, 128.20, 129.10, 146.23, 154.20, 157.47, 161.18, (C-<u>C</u>, aromatics) and 166.28, 166.42 ppm (<u>C</u>=O); FTIR (solid):1778 cm⁻¹ and 1719 cm⁻¹ (C=O), 730 cm⁻¹ (C-N)

A series of polyimides derivatives were prepared according to the reaction stoichiometry outlined in the following table.

Polymer	Monomer (7)	Monomer (8)	Monomer (9)
PI-1	0.5 g	0.66 g	-
	0.001611 mol	0.001611 mol	
PI-2	0.5 g	0.53 g	0.06 g
	0.001611 mol	0.001289 mol	0.0003223 mol
PI-3	0.5 g	0.33 g	0.15 g
	0.001611 mol	0.0008059 mol	0.0008059 mol
PI-4	0.5 g	0.13 g	0.23 g
	0.001611 mol	0.0003223 mol	0.001289 mol
PI-5	0.5 g	-	0.3 g
	0.001611 mol		0.001611 mol

3.5.5 Preparation of Sulfonated Polyimides

A sulfonated polyimide SPI-2 derivative was prepared by the general procedure for the thiolene reaction as outlined by Guan and coworkers.¹⁵ Under a nitrogen atmosphere, polyimide **PI-2** (1 g, 0.314 mmol, n_{inh}: 0.24 dL/g at 25 °C), sodium 3-mercapto-1-propane sulfonate (0.11 g, 0.628 mmol) and 2,2'-azobis(isobutyronitrile) (0.03 g, 0.188 mmol) were added to a 250 mL round bottom flask equipped with a magnetic stirrer bar, followed by the addition of 7.5 mL of a mixed solvent of NMP and DMSO (2:1, v/v). The reaction mixture was heated at 75 °C for 5 days. The polymer product was precipitated into water to give a brown solid. Purification of the brown solid by dialysis with 30 % aqueous acetone for 3 days gave 0.5 g of sulfonated polyimide **SPI-2** as a light brown solid: n_{inh}: 0.25 dL/g at 25 °C; ¹H NMR (300 mHz, CDCl₃, δ , ppm): $\delta = 1.64$ (s, 6H, -C-(CH₃)₂), 1.87 – 1.92 (quin, 2H, CH₂-CH₂-CH₂), 2.15 - 2.20 (t, 2H, (CH₂)₂-CH₂-S), 2.64 - 2.72 (t, (CH₂)₂-CH₂-SO₃Na), 4.44 - 4.48 (t, 1H, R₂-CH-CH₂-S), 4.50 - 4.52 (d, 2H, R₂-CH-CH₂-S), 6.99 - 8.02 ppm (m, 32H, aromatic H); ¹³C NMR (75 mHz, DMSO-d₆, δ , ppm): δ = 31.40 (C-(<u>CH</u>₃)₂), 42.28 (<u>C</u>-(CH₃)₂), 63.58 (<u>C</u>H-CH₂-S-CH₂), 114.20, 134.97, 118.91, 119.15, 125.43, 126.57, 127.18, 127,67, 128.71, 129.57, 146.30, 154.40, 157.10 (C-C, aromatics), 166.88 ppm (C=O); FTIR (solid): 1779 cm⁻¹ and 1720cm⁻¹ (C=O), 1496 and 1590 cm⁻¹ (vs, C=C aromatic), 1024 cm⁻¹ (w, SO₃Na) and 730 cm⁻¹ (C-N).

CHAPTER 4

RESULTS AND DISCUSSION

The synthesis of inexpensive, thermally stable polymeric compounds for use as substrates for the preparation of membranes for water purification and desalination processes, fuel cell technology and nanotechnology has been the focus area of research in industry and academia for the past decade.⁶⁻⁸ In general, poly(ether ether sulfone)s, poly(ether ether ketone)s and polyimides and their derivatives have been extensively used as the engineering polymers of choice for fuel cell technology and water purification applications. The most efficient methods for the preparation of aromatic poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives by step-growth polymerization methods involve electrophilic aromatic substitution polycondensation reactions.⁶⁻⁸

4.1 Synthesis of Poly(ether ether sulfone)s based on Functionalized 1,1-Diphenylethylene Derivatives

Poly(ether ether sulfone)s are useful engineering plastics because of their high thermal and chemical stability. Even in air, degradation is only detected at temperatures above 420 - 450 °C.^{7,8} A variety of synthetic methods for the synthesis of poly(ether ether sulfone)s, which involve electrophilic aromatic substitution, nucleophilic aromatic substitution and metal

catalyzed coupling reactions have been reported in the literature.⁶⁻⁷ Electrophilic aromatic substitution polycondensation reactions were initially used for the syntheses of different poly(ether ether sulfone)s in the presence of low concentrations of Lewis acids and at elevated temperature.^{6, 7} However, poly(ether ether sulfone) derivatives with poor polymer properties were formed. In addition, the synthesis of poly(ether ether sulfone)s via the metal catalyzed coupling method of dihalogenated diaryl sulfone derivatives with silylated bisphenols in the presence of cesium fluoride as catalyst was reported by Kricheldorf and coworkers.³⁰ Furthermore, the base catalyzed nucleophilic aromatic substitution polycondensation reaction between dihalogenated diaryl sulfones and bisphenols provides the most efficient method for the preparation of a wide variety of poly(ether ether sulfone)s.^{6, 7} For example, Gao and Hay³³ prepared poly(ether ether sulfone)s containing the diphenylethylene moiety by the polycondensation reaction of bis(4-chlorophenyl)sulfone with

1,1-bis(4-hydroxyphenyl)ethylene and different bisphenols in the presence of potassium carbonate as catalyst in DMAc/toluene as solvent at 165 °C. In the present study, a series of new poly(ether ether sulfone) derivatives, containing the 1,1-diphenylethylene unit along the polymer backbone were prepared by the step-growth polymerization process using the following synthesis methods:

- (c) The cesium fluoride catalyzed polycondensation reaction of 4,4´-difluorodiphenylsulfone(1) with different mole percentage ratios of silylated bisphenol derivatives,
 - 2,2-bis(4-t-butyldimethylsiloxyphenyl)propane (2) and
 - 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3); and

(d) The potassium carbonate catalyzed nucleophilic aromatic substitution polycondensation reaction of 4,4⁻-difluorodiphenylsulfone (1) with different mole percentage ratios of bisphenol A (4) and 1,1-bis(4-hydroxyphenyl)ethylene (5).

4.1.1 Synthesis and Purification of Monomers

4.1.1.1 Purification of 4,4'-Difluorodiphenylsulfone (1)

Recrystallization of commercially available 4,4[']-difluorodiphenylsulfone (1) from ethanol gave the pure product as white crystals with a melting point of 98 - 99 °C (lit mp¹³⁷ = 98 - 99 °C) and the following structure:



(1)

4.1.1.2 Synthesis of 2,2-Bis(4-*t*-butyldimethylsiloxyphenyl)propane (2)

Thompson and coworkers¹⁴⁸ have reported the synthesis of the silylated bisphenol A derivative, 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) from the reaction of bisphenol A with *t*-butyldimethylsilyl chloride and imidazole hydrochloride in methylene chloride. A synthetic feature of the reaction is the facile removal of the imidazole salt by filtration. Similar procedures for the preparation of silylated bisphenol derivatives were outlined by Quirk and coworkers^{13, 138} and De Meulenaer and coworkers.¹⁴⁰ In the current study, the

preparation of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) was effected by the general procedure outlined by Quirk and Wang,¹³⁸ with modifications. Treatment of bisphenol A with *t*-butyldimethylsilyl chloride in the presence of imidazole and N,N-dimethylformamide gave the crude product as a clear viscous residue. Purification of the product by column chromatography using petroleum ether and ethyl acetate (80/20 = v/v) as eluent gave the clear viscous product. The viscous product solidified on standing to form a white solid, data which was not reported previously in the literature. Recrystallization of the white solid from absolute ethanol gave pure 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) as white crystals in 94 % yield and a melting point of 69 - 72 °C.

The following reaction pathway outlines the synthetic route for the preparation of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**):



The ¹H NMR spectrum (**Figure 1**) of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) shows the following spectral characteristics: (a) a singlet at $\delta = 0.21$ ppm, attributed to the resonance of the twelve protons of the methyl groups attached to the silicon atom; (b) a singlet

at $\delta = 0.99$ ppm, due to the resonance of the eighteen protons of the methyl groups of the tertiary butyl groups attached directly to the silicon atoms; (c) a singlet at $\delta = 1.63$ ppm, ascribed to the resonance of the six methyl protons of the isopropylidene group; and (d) a doublet of doublets at $\delta = 6.72 - 7.10$ ppm, due to the resonance of aromatic protons of the p-substituted benzene rings.

The ¹³C NMR spectrum (**Figure 2**) of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) shows the following characteristic peaks: (a) a peak at $\delta = -4.40$ ppm, attributed to the resonance of the four carbon atoms of the methyl groups attached to the silicon atom; (b) signals at $\delta = 18.16$ ppm and 25.69 ppm, attributed to the resonance of the tertiary carbon atom and the three carbon atoms of the methyl groups of each t-butyl moiety, respectively; and (c) peaks at 31.10 ppm and 41.72 ppm, corresponding to the resonance of the primary and quaternary carbon atoms of the isopropylidene group, respectively. The peaks between 119.17 ppm and 153.25 ppm correspond to the resonances of the different carbon atoms of the two phenyl rings.

The FTIR spectrum (**Figure 3**) of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) shows an absorption band at 1259 cm⁻¹, which is attributed to the vibration modes of Si-C bonds of the Si(CH₃)₂ groups.

A modified synthetic route for the preparation of the silylated bisphenol A derivative, 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) is reported. After purification of the product by column chromatography, the clear resultant viscous product solidified on standing to form a white solid. Recrystallization of the white solid from absolute ethanol gave pure 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) as white crystals with a melting point of 69 - 72 °C. The structure of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) was confirmed by ¹H NMR and ¹³C NMR spectrometry and FTIR spectroscopy.

4.1.1.3 Synthesis of 1,1-Bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3)

The general synthetic route for the preparation of symmetrical disubstituted 1,1diphenylethylene derivatives involves the conversion of the appropriate benzophenone precursor to the corresponding carbinol intermediate, followed by the thermal or acid catalyzed dehydration of the intermediate carbinol to produce the corresponding disubstituted 1,1-diphenylethylene derivative.^{149, 150} A more efficient method for the direct conversion of disubstituted benzophenones to the corresponding disubstituted 1,1-diphenylethylene derivatives is via the Wittig reaction with phosphoryl ylides^{30, 138} or the Tebbe reagent.¹⁵¹ Recently, Raut and coworkers¹⁵² developed a new method for the preparation of disubstituted 1,1-diphenylethylene derivatives by the copper-catalyzed C-H addition of arenes with aryl acetylenes.

The preparation of 1,1-bis[4-(t-butyldimethylsiloxy)phenyl]ethylene (**3**) was first reported by Quirk and Wang^{13, 138} using the following method:

(a) Treatment of 4,4´-dihydroxybenzophenone with *t*-butyldimethylsilyl chloride in the presence of imidazole and N,N-dimethylformamide to form the intermediate
 4,4´-bis(*t*-butyldimethylsiloxy)benzophenone derivative; and

(b) The conversion of 4,4 -bis(*t*-butyldimethylsiloxy)benzophenone to

1,1-bis(4-*t*-butyldimethylsiloxyphenyl)ethylene (**3**) via the Wittig reaction.

However, the intermediate product, 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone, was only obtained as a clear viscous liquid. Furthermore, Hejaz and coworkers¹⁵³ reported the synthesis of the intermediate product, 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone which was isolated as a solid, but no melting point data was recorded.

The current research work reports the high yield synthesis pathway for the preparation of 1,1bis[4-(t-butyldimethylsiloxy)phenyl]ethylene (**3**) as a pure, white solid using the procedure outlined by Quirk and Wang,¹³⁸ with modifications. The synthetic route involved the following steps:

- (a) The preparation of 4,4´-bis(*t*-butyldimethylsiloxy)benzophenone using4,4´-dihydroxybenzophenone as the starting material; and
- (b) The direct conversion of 4,4'-bis(t-butyldimethylsiloxy)benzophenone to
 1,1-bis[4-(t-butyldimethylsiloxy)phenyl]ethylene (3) via the classic Wittig reaction as outlined in the following reaction scheme:



Preparation of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone:

The intermediate product, 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone, which was obtained after treatment of 4,4'-dihydroxybenzophenone with *t*-butyldimethylsilyl chloride in the presence of imidazole in N,N-dimethylformamide for 3 hours, was purified by column chromatography to give 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone as white solid. Recrystallization of the white solid from absolute ethanol gave pure 4,4'-bis(*t*- butyldimethylsiloxy)benzophenone as fine white crystals in 66 % yield with a melting point of 52.5 - 55.7 °C.

The ¹H NMR spectrum (**Figure 4**) of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone shows the following spectral characteristics: (a) a singlet at $\delta = 0.24$ ppm, attributed to the resonance of the protons of the four methyl groups attached directly to the silicon atom; (b) a singlet at $\delta = 0.99$ ppm, due to the resonance of the protons of the six methyl groups of the t-butyl moieties attached directly to the silicon atom. The doublet of doublets at $\delta = 6.88 - 7.74$ ppm, corresponding to the resonance of the aromatic protons of the phenyl rings, is characteristic of p-substituted benzene rings.

The ¹³C NMR spectrum (**Figure 5**) of 4,4'-bis(*t*-buyldimethylsiloxy)benzophenone shows a peak at $\delta = -4.40$ ppm, attributed to the resonance of the carbon atoms of the Si-(CH₃)₂ groups. The peaks at $\delta = 18.19$ ppm and 25.56 ppm correspond to the resonance of the tertiary carbon atom and the carbon atoms of the three methyl groups of each t-butyl moiety, respectively. The peak at 194.60 ppm corresponds to the resonance of the carbonyl carbon of the benzophenone nucleus.

The FTIR spectrum (**Figure 6**) of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone shows an absorption band at 1272 cm⁻¹, due to the presence of the stretching modes of the Si-C bonds of the Si-(CH₃)₂ groups. The strong adsorption band at 1695 cm⁻¹ is due to the C=O stretching modes of the benzophenone derivative. The spectroscopy data of the intermediate 4,4'-bis(*t*-

butyldimethylsiloxy)benzophenone derivative is in good agreement with the data reported by Quirk and Wang.¹³⁸

The modified synthesis pathway for the conversion of the 4,4[']-dihydroxybenzophenone to 4,4[']-bis(*t*-butyldimethylsiloxy)benzophenone afforded the pure product as a white crystalline solid with a melting point of 52.5 - 55.7 °C.

Preparation of 1,1-Bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3):

The direct conversion of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone to the desired product, 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) was effected by the classic Wittig reaction with phosphoryl ylides. The phosphoryl ylide was generated *in situ* from the reaction of methyllithium with methyltriphenylphosphonium bromide at room temperature. The rapid treatment of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone with the phosphoryl ylide gave a clear viscous product which solidified on standing to give a white solid. Recrystallization of the resultant white solid from absolute ethanol gave the target molecule, 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) as white crystals in 63 % yield with a melting point of 55.9 - 56.4 °C (lit mp¹³⁸ = 56 - 57.5 °C).

The ¹H NMR spectrum (**Figure 7**) of 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) exhibits a singlet at $\delta = 0.21$ ppm, attributed to the resonance of the twelve protons of the methyl groups attached directly to the two silicon atoms. The singlet at $\delta = 0.99$ ppm is due to the resonance of the protons of the three methyl groups of each t-butyl moiety attached directly to the silicon atoms. The singlet at $\delta = 5.28$ ppm corresponds to the resonance of the

protons of the C=CH₂ olefin group and the doublet of doublets at δ = 6.77 - 7.20 ppm is due to the resonance of the aromatic protons of the phenyl rings and is characteristic of p-substituted benzene rings.

The ¹³C NMR spectrum (**Figure 8**) of 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) shows the presence of a signal at $\delta = -4.38$ ppm, due to the resonance of the carbon atoms of the methyl groups attached directly to the silicon atoms. The signals at 18.21 ppm and 25.69 ppm are due to the resonance of the two tertiary carbon atoms and the resonance of the carbon atoms of the three methyl groups of the t-butyl groups, respectively. The peaks at 111.66 ppm and 134.81 ppm correspond to the resonance of the C-1 (CH₂=CR₂) and C-2 (CH₂=<u>C</u>R₂) olefin carbon atoms of the CH₂= CR₂ group, respectively. The absence of a peak at 194.60 ppm, due to the resonance of carbonyl carbon atoms confirms the complete conversion of the benzophenone precursor to the 1,1-diphenylethylene derivative via the Wittig reaction.

The FTIR spectrum (**Figure 9**) of 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) shows the presence of two absorption bands at 1265 cm⁻¹ and 889 cm⁻¹, which corresponds to the stretching modes of the Si-C and C-H bonds of the siloxyl and olefin groups, respectively. The absence of an adsorption band at 1695 cm⁻¹ indicates the complete Wittig reaction with 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone and subsequent product formation without any benzophenone impurity.

The synthesis of 1,1-bis[4-(t-butyldimethylsiloxy)phenyl]ethylene (**3**) was performed via a two step synthesis method using 4,4⁻-dihydroxybenzophenone as starting material. The high

yield formation of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone as white crystals was effected by the reaction of 4,4'-dihydroxybenzophenone with *t*-butyldimethylsilyl chloride. The subsequent Wittig reaction of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone with an appropriate phosphoryl ylide afforded 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) as white crystals. The structure of 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) was confirmed by ¹H NMR and ¹³C NMR spectrometry and FTIR analysis and the spectroscopic data corresponds well with the data reported by Quirk and Wang.¹³⁸

4.1.1.4 Purification of Bisphenol A (4)

Recrystallization of commercially available bisphenol A from toluene afforded pure bisphenol A (4) as white crystals with a melting point of 156 - 158 °C (lit $mp^{140} = 156 - 158$ °C) and the following structure:



4.1.1.5 Synthesis of 1,1-Bis(4-hydroxyphenyl)ethylene (5)

The general synthetic pathway for the preparation of symmetrical disubstituted 1,1diphenylethylene compounds from appropriate benzophenone precursors involves two methods:

- (a) The conversion of an appropriate disubstituted benzophenone precursor to a carbinol intermediate product, followed by the spontaneous thermal or acid catalyzed dehydration of the intermediate carbinol^{149, 150} to afford the corresponding disubstituted 1,1-diphenylethylene derivative; and
- (b) The direct conversion of an appropriate disubstituted benzophenone precursor to the corresponding disubstituted 1,1-diphenylethylene derivative via the classic Wittig reaction using phosphoryl ylides^{30, 138} or the Tebbe reagent.¹⁵¹

In addition, disubstituted 1,1-diphenylethylene derivatives can be efficiently prepared by functional group transformation reactions using the appropriate disubstituted 1,1diphenylethylene derivative as the starting material. For example, Hay and Gao,³³ Sonawane and coworkers¹⁵⁴ as well as Jian and coworkers¹³¹ reported the preparation of 1,1-bis(4hydroxyphenyl)ethylene (**5**) by the demethylation of the 1,1-bis(4-methoxyphenyl)ethylene precursor.

The current research outlines a new method for the preparation of 1,1-bis(4hydroxyphenyl)ethylene (5) using 4,4´-dihydroxybenzophenone as substrate via a synthesis route which involves three steps:

- (a) The preparation of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone from 4,4'dihydroxybenzophenone;
- (b) The direct conversion of 4,4´-bis(*t*-butyldimethylsiloxy)benzophenone to 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3) via the classic Wittig reaction; and

(c) The conversion of 1,1-bis(4-*t*-butyldimethylsiloxyphenyl)ethylene (3) to the corresponding dihydroxyl 1,1-diphenylethylene derivative, 1,1-bis(4-hydroxyphenyl)ethylene (5) by removal of the silyl groups by the reaction with tetrabutylammonium fluoride according to the procedure outlined by De Meulenaer and coworkers¹⁴⁰ as depicted in the following reaction scheme:



The disiloxy derivative, 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) was treated with tetrabutylammonium fluoride (TBAF) to give 1,1-bis(4-hydroxyphenyl)ethylene (**5**). The reaction of 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) with tetrabutylammonium fluoride proceeded at room temperature for 2 hours. Removal of the solvent afforded the crude product as a pale yellow solid. Recrystallization of the yellow solid from ethanol/water (1/18, v/v) gave 1,1-bis(4-hydroxyphenyl)ethylene (**5**) as fine yellow crystals in 62 % yield with a melting point of 151.1 - 152.8 °C (lit mp¹⁴¹ = 150 – 152 °C).

The ¹H NMR spectrum (**Figure 10**) of 1,1-bis(4-hydroxyphenyl)ethylene (**5**) exhibits a singlet at $\delta = 5.17$ ppm, which is due to the resonance to the protons of the olefinic C=C<u>H</u>₂ group. The singlet at $\delta = 9.50$ ppm corresponds to the resonance of the protons of the two O<u>H</u> groups. The doublet of doublets at $\delta = 6.71 - 7.21$ ppm is assigned to the resonance of the protons of the aromatic rings and is characteristic of the p-substituted benzene rings. The absence of any peaks at 0.21 ppm and 0.98 ppm confirms the complete removal of the t-butyldimethylsilyl groups.

The ¹³C NMR spectrum (**Figure 11**) of 1,1-bis(4-hydroxyphenyl)ethylene (**5**) shows characteristic peaks at $\delta = 110.71$ ppm and 132.44 ppm, assigned to the resonance of the carbon atoms of the ethylene group. The peak at $\delta = 110.71$ ppm correspond to the resonance of terminal =<u>C</u>H₂ carbon atom of the olefin group and the peak at 132.44 ppm is due to the resonance of the olefinic carbon atom of the CH₂=<u>C</u>R₂ group. The peaks between $\delta = 115.47$ ppm and 157.69 ppm are attributed to the resonance of the different aromatic carbon atoms of the para substituted benzene rings.

The FTIR spectrum (**Figure 12**) of 1,1-bis(4-hydroxyphenyl)ethylene (**5**) shows the presence of strong absorption bands at 3240 cm⁻¹ and 892 cm⁻¹, due to the O-H and C-H stretching modes of the OH and C=CH₂ groups, respectively.

The results show that treatment of 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**), with tetrabutylammonium fluoride (TBAF) in THF for 12 hours provides a new facile method for the removal of the t-butyldimethylsilyl groups to afford 1,1-bis(4-hydroxyphenyl)ethylene (**5**)

in high yields. The structure of 1,1-bis(4-hydroxyphenyl)ethylene (**5**) was confirmed by ¹H NMR and ¹³C NMR spectrometry and FTIR analysis and the spectroscopic data is consistent with the data reported by Wang and coworkers¹³¹ and Gao and Hay.³³

4.1.2 Synthesis of Poly(ether ether sulfone)s by Step-Growth Polymerization Methods

4.1.2.1 The Cesium Fluoride Catalyzed Polymerization of Dihalogenated Diaryl Sulfones with Silylated Bisphenols.

The general method for the synthesis of poly(ether ether sulfone)s by step-growth polymerization using dihalogenated diaryl sulfones and silylated bisphenols as monomers in the presence of cesium fluoride as catalyst was developed by Kricheldorf and coworkers.³⁰ Similarly, a series of new poly(ether ether sulfone)s were prepared by the cesium fluoride catalyzed polymerization of 4,4'-difluorodiphenylsulfone (**1**) with different mole percentage ratios of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) and 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) as the silylated bisphenols according to the following reaction scheme:



In a typical polycondensation experiment, 4,4'-difluorodiphenylsulfone (1) was treated with a mole percentage ratio of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (2): 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3) = 80:20 in the presence of cesium fluoride as catalyst in NMP at 150 °C for 12 hours. The polymer product was precipitated into methanol, filtered and vacuum dried to afford the poly(ether ether sulfone) copolymer derivative **PSU-2** as a white solid.

The different poly(ether ether sulfone) derivatives were prepared using the stoichiometric ratios of reactants as outlined in the following table:

Polymer	Monomer (1)	Monomer (2)	Monomer (3)
	mol %	mol %	mol %
PSU-1	100	100	-
PSU-2	100	80	20
PSU-3	100	50	50
PSU-4	100	20	80
PSU-5	100	-	100

4.1.2.2 The Potassium Carbonate Catalyzed Polymerization of Dihalogenated Diaryl Sulfones with Bisphenols.

The preparation of poly(ether ether sulfone)s by the base catalyzed nucleophilic aromatic substitution polycondensation reactions have been reported in the literature.^{6, 7, 33} Similarly, the syntheses of new poly(ether ether sulfone) derivatives by step-growth polymerization by the base catalyzed nucleophilic substitution reactions of dihalogenated diaryl sulfones with bisphenols were conducted according to the procedure described by Gao and Hay.³³ The synthesis of a series of new poly(ether ether sulfone)s was effected by the potassium carbonate catalyzed polymerization of 4,4'-difluorodiphenylsulfone (1) with different mole percentage ratios of bisphenol A (4) and 1,1-bis(4-hydroxyphenyl)ethylene (5) according to the following reaction pathway:



In a typical polycondensation experiment, the poly(ether ether sulfone) derivative **PSU-7** was prepared by the polycondensation method involving the nucleophilic aromatic polycondensation reaction of 4,4'-difluorodiphenylsulfone (1) with a percentage mole ratio of bisphenol A (4): 1,1-bis(4-hydroxyphenyl)ethylene (5) = 80:20 in the presence of potassium carbonate as catalyst at 165 °C in dimethylacetamide for 3 hours with toluene as the azeotropic agent. The polymer product was coagulated into methanol, filtered and vacuum dried to afford the poly(ether ether sulfone) copolymer derivative **PSU-7** as a white solid.

The experimental details for the preparation of the different poly(ether ether sulfone) derivatives are outlined in the following table:

Polymer	Monomer (1)	Monomer (4)	Monomer (5)
	mol %	mol %	mol %
PSU-6	100	100	0
PSU-7	100	80	20
PSU-8	100	50	50
PSU-9	100	20	80
PSU-10	100	0	100

4.1.3 Characterization of the Different Poly(ether ether sulfone) Derivatives

To evaluate the effect of the introduction of the 1,1-diphenylethylene unit along the polymer backbone, a series of new poly(ether ether sulfone) derivatives were prepared by two different methods:

- (a) Method 1: The preparation of poly(ether ether sulfone)s by the cesium fluoride catalyzed polycondensation reactions of dihalogenated diaryl sulfones with silylated bisphenols; and
- (b) **Method 2**: The synthesis of poly(ether ether sulfone)s by the potassium carbonate catalyzed polycondensation of dihalogenated diaryl sulfones with bisphenols.

The synthesis and characterization of poly(ether ether sulfone) **PSU-2** as a representative sample is discussed in detail and compared with the other poly(ether ether sulfone) samples, where applicable. In a typical experiment, the preparation of poly(ether ether sulfone) derivative **PSU-2** was effected by the catalytic arylation reaction of 4,4′-

difluorodiphenylsulfone (1) with 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (2) and 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3) using cesium fluoride as the catalyst in NMP at 150 °C for 12 hours. The poly(ether ether sulfone) derivative **PSU-2** was prepared using mole percentage ratios of [1]:[2]:[3] = [100]:[80]:[20] in the monomer feed. The polymer product was isolated by precipitation into methanol, filtered and vacuum dried to afford poly(ether ether sulfone) derivative **PSU-2** as a white solid.

The size exclusion chromatogram (**Figure 13**) of poly(ether ether sulfone) derivative **PSU-2** shows a monomodal molecular weight distribution curve with $\overline{M}_n = 9.6 \times 10^3$ g/mol and $\overline{M}_w/\overline{M}_n = 1.23$. The following table provides size exclusion chromatography characterization data for different poly(ether ether sulfone) derivatives:

Polymer	$\overline{\mathbf{M}}_{\mathbf{n}}$	$\overline{\mathbf{M}}_{\mathbf{w}}$	$\overline{\mathbf{M}}_{w}/\overline{\mathbf{M}}_{n}$
	×10 ⁻³ g/mol	×10 ⁻³ g/mol	
PSU-1	8.9	10.7	1.20
PSU-2	9.6	11.8	1.23
PSU-3	12.5	17.3	1.38
PSU-4	13.2	18.1	1.37
PSU-5	21.1	25.32	1.20
PSU-6	13.6	17.7	1.30
PSU-7	14.7	18.1	1.23
PSU-8	16.3	19.7	1.20
PSU-9	17.9	22.2	1.24
PSU-10	30.4	40.4	1.32

Well-defined poly(ether ether sulfone) derivatives with the number average molecular weights between $8.9 \times 10^3 - 30.4 \times 10^3$ g/mol and narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n = 1.20 - 1.38$) were obtained.

The \overline{M}_n values of the 1,1-diphenylethylene based homopolymers, **PSU-5** and **PSU-10** obtained by the polycondensation reaction of 4,4'-difluorodiphenylsulfone (1) with the 1,1diphenylethylene derivatives, are significantly higher than the \overline{M}_n values of the bisphenol A based homopolymers **PSU-1** and **PSU-6**, respectively. In addition, the size exclusion chromatography results show that the number average molecular weights of the different poly(ether ether sulfone) derivatives increases with increasing content of the 1,1-bis[4-(*t*butyldimethylsiloxy)phenyl]ethylene (3) monomer, irrespective of the synthesis method.

The chemical structure of each poly(ether ether sulfone) derivative was confirmed by ¹H NMR and ¹³C NMR spectrometry and FTIR analyses. The ¹H NMR spectrum (**Figure 14**) of the poly(ether ether sulfone) derivative **PSU-2** exhibits a singlet at $\delta = 1.68$ ppm, due to the resonance of the protons of the methyl groups of the bisphenol A units along the polymer backbone. The singlet at $\delta = 5.44$ ppm, attributed to the proton resonances of the C=CH₂ group, confirms the presence of the 1,1-diphenylethylene unit along the polymer backbone. A multiplet at $\delta = 6.91 - 7.88$ ppm corresponds to the resonance of the aromatic protons from the different benzene rings along the polymer backbone. The ¹³C NMR spectrum (**Figure 15**) of poly(ether ether sulfone) derivative **PSU-2**, shows a signal at $\delta = 114.62$ ppm, due to the resonance of the C=<u>C</u>H₂ carbon atom, which confirms the presence of the C=CH₂ group along the polymer backbone. The absence of any peaks associated with the resonance of the carbon atoms of the silyl groups of the monomer precursor confirms complete step-growth polymerization process and the absence of contamination by residual monomer.

The FTIR spectrum (**Figure 16**) of poly(ether ether sulfone) derivative **PSU-2** shows an absorption band at 1149 cm⁻¹, attributed to the presence of the S=O stretching modes of the sulfonyl groups along the polymer backbone. The absorption bands at 1487 and 1584 cm⁻¹ are attributed to the C=C stretching vibrations of the aromatic rings within the polymer chain.

The thermal stability of each poly(ether ether sulfone) derivative was determined by thermogravimetric analysis. **Figure 17** shows a typical TGA curve the poly(ether ether sulfone) derivative **PSU-2.** The thermal degradation pattern of poly(ether ether sulfone) **PSU-2** occurs via a two step process: (a) a weight loss of 0.26 % between 100 °C – 150 °C, due to the loss of moisture or solvent from the sample; and (b) a rapid weight loss of 61.06 % between 450 °C - 550 °C, due to the degradation of the polymer chain. In addition, a residual weight of 33 % was retained up to 600 °C. In general, the 1,1-diphenylethylene based poly(ether ether sulfone)s are thermally less stable than the bisphenol A based poly(ether ether sulfone)s and the thermal stability decreases with the increasing content of the rigid 1,1-diphenylethylene unit. All poly(ether ether sulfone) samples undergo thermal degradation of

the polymer chain above 450 °C, indicating good thermal stability for each polymer sample. The TGA data of each poly(ether ether sulfone) derivative is depicted in the following table:

Polymer	T ₁₀ (°C)	T _d	W _{550°C}
PSU-1	511	455	51.60
PSU-2	494	450	50.06
PSU-3	490	437	38.02
PSU-4	488	408	36.35
PSU-5	483	380	32.53
PSU-6	516	448	56.68
PSU-7	508	446	50.70
PSU-8	505	439	41.57
PSU-9	472	401	36.71
PSU-10	471	388	35.56

where T_{10} represents the 10 % weight loss temperature, T_d depicts the onset temperature for polymer chain decomposition and $W_{550^{\circ}C}$ represents the percentage weight loss at 550°C, the temperature at which complete polymer degradation is observed.

The glass transition temperature of each poly(ether ether sulfone) sample was determined by DSC analysis. The DSC curve for poly(ether ether sulfone) derivative **PSU-2** is shown in **Figure 18**. The onset of molecular motion occurs at a temperature of 165 °C and a glass transition temperature of $T_g = 168$ °C was recorded. The DSC analysis of poly(ether ether

sulfone) derivative **PSU-2**, shows that the introduction of 20 mole percentage of the 1,1diphenylethylene unit increases the T_g value when compared to the T_g value of the corresponding homopolymer **PSU-1**. The introduction of the planar, rigid non-linear 1,1diphenylethylene unit along the polymer backbone increases steric hindrance to intersegmental motion, thus reduces chain mobility and flexibility and increases the T_g value of the copolymer **PSU-2** relative to the pure homopolymer **PSU-1**. Due to the introduction of the rigid, 1,1-diphenylethylene unit along the polymer backbone, which increases polymer chain stiffness, the T_g values of the 1,1-diphenylethylene based homopolymers **PSU-5** and **PSU-10**, are significantly higher than the T_g values of the bisphenol A based homopolymers **PSU-1** and **PSU-6**, respectively. The T_g values for different poly(ether ether sulfone) derivatives are depicted in the following table:

Polymer	T _g (°C)
PSU-1	156
PSU-2	168
PSU-3	172
PSU-4	190
PSU-5	199
PSU-6	151
PSU-7	170
PSU-8	172
PSU-9	176
PSU-10	180

The T_g values for the different poly(ether ether sulfone) derivatives range between 151 °C and 199 °C. For a given series, the T_g values of the different poly(ether ether sulfone) derivatives increase with increasing content of the 1,1-diphenylethylene content unit along the polymer backbone. The T_g results show that all the samples displayed a single T_g value. No melting endotherm and crystallization temperature were observed between the recorded temperatures of 25 °C to 400 °C.

Dense membranes obtained from the different poly(ether ether sulfone) derivatives were prepared by the spin coating method and the membrane properties of the different polymers were characterized by atomic force microscopy. The three dimensional AFM image (**Figure 19**) of the surface of the membrane of poly(ether ether sulfone) derivative **PSU-2** displays non-aligned nodule groups separated by pores of different sizes. The surface of the membrane is not smooth, but display varying degrees of surface roughness and porosity of different pore sizes. The dark regions, low valleys and depressions in the AFM image are attributed to the pores of the polymer, whereas the light regions, high peaks and bright areas correspond to the spherical macromolecular aggregates.¹⁵⁵⁻¹⁵⁷ The topographical image of the **PSU-2** sample shows a surface roughness value of 9.4 nm. The membrane surface shows that the variation between the light and dark regions is small and constant throughout the membrane region. The pore sizes vary between 263.67 to 808.6 nm
The morphology of each poly(ether ether sulfone) sample in the powder form was further investigated by transmission electron microscopy analysis.¹⁵⁸⁻¹⁶⁰ Figure 20 shows the TEM micrograph of poly(ether ether sulfone) derivative **PSU-2** which displays polymer aggregates of different shapes and sizes.

The X-ray diffraction patterns for the different poly(ether ether sulfone) derivatives in the powder form were recorded to determine the degree of crystallinity of each polymer sample. Typical broad amorphous bands with some crystallinity were observed for each polymer sample. The X-ray diffraction pattern (**Figure 21**) of poly(ether ether sulfone) derivative, **PSU-2** shows the presence of broad peaks between $2\theta = 18 - 20^{\circ}$ and $40 - 45^{\circ}$ which are typical of amorphous and crystalline regions, respectively and indicates that the polymer structure for poly(ether ether sulfone) **PSU-2** is predominantly amorphous with some degree of crystallinity. The large amounts of ether linkages along the polymer backbone considerably lower the energy of internal rotation of the polymer chain, thus reducing the crystallinity of the polymer, ¹⁶¹⁻¹⁶³ whereas the 20 % rigid 1,1-diphenylethylene units along the polymer backbone promotes polymer crystal growth.

Elemental analysis of the poly(ether ether sulfone) derivative **PSU-2** was determined by elemental analysis and gave the following data:

Elemental analysis (calculated): C, 73.47; H, 5.16; O, 14.24; S, 7.13.

Elemental analysis (found) : C, 71.50; H, 4.96; S, 6.96. The elemental analysis data confirms the formation of the poly(ether ether sulfone) derivative **PSU-2**. A series of new, well-defined poly(ether ether sulfone) derivatives were prepared by two methods, namely (a) the catalytic arylation polycondensation reactions between dihalogenated diaryl sulfones and silylated bisphenols, and (b) the base catalyzed polycondensation reactions between dihalogenated diaryl sulfones with bisphenols. Due to the increased content of 1,1diphenylethylene units within the polymer backbone, the number average molecular weights of the resultant polymers increase accordingly. The thermal stability of the resultant polymers decreases with the regiospecific introduction of the 1,1-diphenylethylene unit along the polymer chain for the different poly(ether ether sulfone) derivatives. In addition, the T_g values of the different poly(ether ether sulfone) derivatives increase with increasing 1,1diphenylethylene content when compared to the parent poly(ether ether sulfone).

4.2 Synthesis and Characterization of Sulfonated Poly(ether ether sulfone)s

A plethora of synthetic methods for the preparation of sulfonated poly(ether ether sulfone) derivatives by different post-polymerization sulfonation methods have been reported in the literature.⁴⁹ However, the use of thiol-ene chemistry in post-polymerization functionalization reactions, which was recently introduced to the area of polymer synthesis by the late Charles Hoyle and his coworkers,^{63, 64} has not been widely employed as a method for the preparation of sulfonated poly(ether ether sulfone) derivatives. The classic thiol-ene reaction involves the addition of a S-H bond across a double bond by either a free radical or ionic mechanism. Post-polymerization functionalization of different polymers containing sites of unsaturation can be effected by the thiol-ene method under different reaction conditions and in the presence of different catalysts. Jannasch and coworkers⁷⁴ reported the synthesis of functionalized

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poly(ether ether sulfone) via the thiol-ene method from the reaction of poly(ether ether sulfone) bearing the undecenoyl side chain with 2-(2-benzimidazoyl)ethanethiol and AIBN in THF at 60 °C. The reaction proceeded in such a manner that no detectable polymer degradation was observed.

In the current study, due to the regiospecific introduction of the $C=CH_2$ group along the polymer backbone in the 1,1-diphenylethylene based different poly(ether ether sulfone) derivatives **PSU-2** to **PSU-5** and **PSU-7** to **PSU-10**, a new sulfonation method, which utilizes the classic thiol-ene reaction, was employed to prepare new sulfonated poly(ether ether sulfone) derivatives for evaluation as polymeric precursors for membranes in fuel cell technology.

In a typical procedure, a new sulfonated poly(ether ether sulfone) derivative **SPSU-2** was prepared via the thiol-ene method according to the following synthesis pathway:



The design of the sulfonation reaction using the thiol-ene method was to target the 1,1diphenylethylene site on the polymer backbone and allow the regiospecific introduction of the sulfonate groups along the polymer chain as well as the control of the degree of sulfonation. In a one pot reaction, the poly(ether ether sulfone) derivative **PSU-2** was treated with sodium 3-mercapto-1-propane sulfonate in the presence of AIBN as the initiator at 75 °C for 5 days. The polymer product was coagulated into water, filtered and subsequently subjected to a dialysis process with 30 % aqueous acetone to afford sulfonated poly(ether ether sulfone) **SPSU-2** as a white solid.

The size exclusion chromatogram (**Figure 22**) of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** shows a monomodal molecular weight distribution curve with a $\overline{M}_n =$ 10.8×10^3 g/mol and $\overline{M}_w/\overline{M}_n = 1.20$. The \overline{M}_n value of the sulfonated poly(ether ether sulfone) **SPSU-2** is slightly higher compared to the \overline{M}_n of the poly(ether ether sulfone) derivative **PSU-2** precursor.

The ¹H NMR spectrum (**Figure 23**) of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** shows a singlet at $\delta = 1.62$ ppm, which corresponds to the resonance of the protons of the methyl groups of the isopropylidene group of the bisphenol A unit and confirms that the bisphenol A moiety along the polymer backbone was not affected by the thiol-ene reaction. In addition, the ¹H NMR spectrum shows the following characteristic peaks which are associated with the introduction of the mercaptopropyl sulfonate group pendant to the polymer backbone:^{15, 69, 70, 132} (a) a quintet at $\delta = 1.87 - 1.92$ ppm, due to the resonance of the protons of the CH₂-CH₂-CH₂-SO₃Na group; (b) a triplet at $\delta = 2.15 - 2.17$ ppm, attributed to the

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resonance of the protons of the CH₂-C<u>H</u>₂-S group; (c) a triplet at $\delta = 2.66 - 2.74$ ppm, assigned to the resonance of the protons on the carbon α to the sodium sulfonate group (CH₂)₂-C<u>H</u>₂-SO₃Na; (d) a triplet at $\delta = 4.35 - 4.39$ ppm, assigned to the resonance of the methine proton of the R₂-C<u>H</u>-CH₂-S group (e) a doublet at $\delta = 4.44 - 4.46$ ppm, due to the resonance of the protons of the R₂-CH-C<u>H</u>₂-S group. The absence of a peak at $\delta = 5.44$ ppm, due to the resonance of the proton of the C=C<u>H</u>₂ group of the 1,1-diphenylethylene unit within the **PSU-2** precursor, confirms the complete sulfonation of poly(ether ether sulfone) **PSU-2** via the thiol-ene reaction.

The ¹³C NMR spectrum (**Figure 24**) of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** shows characteristic peaks at $\delta = 25.91$ ppm (CH₂-<u>C</u>H₂-CH₂SO₃Na), $\delta = 30.64$ ppm (CH₂-<u>C</u>H₂-S), $\delta = 31$ (C(<u>C</u>H₃)₂), $\delta = 42.43$ (<u>C</u>-(CH₃)₂) and $\delta = 63.59$ ppm (R₂<u>C</u>H-CH₂-S), which confirms the regiospecific introduction of the sulfonating agent pendant to the polymer backbone as the result of the thiol-ene reaction with the 1,1-diphenylethylene moiety along the polymer chain.

The FTIR spectrum (**Figure 25**) of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** shows an absorption band at 1027 cm⁻¹, corresponding to the S=O stretching modes of the sulfonate groups. The absorption band at 1151 cm⁻¹, is due to the characteristic stretching modes of the sulfonyl groups along the backbone of the sulfonated poly(ether ether sulfone) derivative **SPSU-2**. The absorption bands at 1488 cm⁻¹ and 1585 cm⁻¹ are attributed to the vibrational stretching modes of the C=C bonds of the aromatic rings along the polymer chain.

The thermal stability of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** was determined by thermogravimetric analysis. The TGA curve (**Figure 26**) of sulfonated poly(ether ether sulfone) **SPSU-2** exhibits a three phase degradation pattern with the following characteristics: (a) an initial weight loss of 1.26 % between 75 °C - 150 °C, due to the loss of moisture and residual solvent trapped in the polymer, (b) a weight loss of 1.29 % between 320 °C - 350 °C, which is assigned to the decomposition of the pendant substituents containing sulfonate groups, and (c) a rapid weight loss of 34 % between 425 °C- 550 °C, attributed to the degradation of the polymer backbone. The TGA data shows that the sulfonated poly(ether ether sulfone) **SPSU-2** derivative is thermally less stable than the poly(ether ether sulfone) precursor **PSU-2**, between 100 °C – 550 °C, due to the introduction of alkyl sulfonate groups along the polymer chain which increases the amorphous nature of the sulfonate polymer.¹¹

The glass transition temperature of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** was determined by differential scanning calorimetry. The DSC curve (**Figure 27**) of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** shows a glass transition temperature of 192 °C. The T_g value of **SPSU-2** is higher than the T_g value of the poly(ether ether sulfone) precursor **PSU-2** (T_g = 168 °C) due to the introduction of the pendant propyl sulfonate groups along the polymer backbone which increase polymer chain rigidity. The interchain association of the sulfonate groups reduces the chain flexibility and increases the rigidity of the polymer chains, thus increasing the T_g value of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** relative to the poly(ether ether sulfone) **PSU-2** precursor.

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The dense membrane obtained from the sulfonated poly(ether ether sulfone) derivative **SPSU-2** was characterized by atomic force microscopy. **Figure 28** representing the three dimensional AFM image of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** membrane shows non-aligned polymer aggregates. The sulfonated poly(ether ether sulfone) derivative **SPSU-2** is a relatively smooth membrane as shown by the membrane roughness of value of 1.11 nm. Well-defined pores with pore sizes between 70.3 – 152.3 nm are displayed by dark regions, low valleys and depressions in the AFM image.

The morphology of the sulfonated poly(ether ether sulfone) derivative **SPSU-2**, in the powder form, was evaluated by transmission electron microscopy analysis. The TEM image (**Figure 29**) of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** reveals dark domains, attributed to the polymer matrix which contains the non-polar amorphous polymer and a low concentration of polar hydrophilic sulfonate regions.

The X–ray diffraction analysis data of the sulfonated poly(ether ether sulfone) derivative, **SPSU-2** was recorded to determine the degree of crystallinity of the polymer in the powder form. The analysis of the XRD spectrum (**Figure 30**) of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** reveals that the polymer structure is predominantly amorphous with the characteristic broad amorphous peak observed between $2\theta = 20^{\circ} - 25^{\circ}$.¹⁶⁰⁻¹⁶² The amorphous nature of the resultant sulfonated polymer is attributed to the introduction of alkyl sulfonate groups along the polymer backbone, a characteristic requirement of an excellent material for use in polymer electrolyte membrane fuel cells.¹⁵

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Elemental analysis of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** as determined by elemental analysis gave the following data:

Elemental analysis (calculated): C, 64.66; H, 4.96; O, 16.34; S, 11.91.

Elemental analysis (found) : C, 68.73; H, 5.04; S, 7.78.

The elemental analysis data confirms the formation of sulfonated poly(ether ether sulfone) derivative **SPSU-2** and is consistent with the introduction of 20 % 1,1-diphenyethylene units along the polymer chain in the poly(ether ether sulfone) precursor **PSU-2** and the subsequent sulfonation reaction with the 1,1-diphenyethylene unit to afford the sulfonated poly(ether ether sulfone) derivative **SPSU-2**.

The ion exchange capacity of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** was determined by using the difference in the weight percentage contents of sulphur in the sulfonated poly(ether ether sulfone) **SPSU-2** and the poly(ether ether sulfone) **PSU-2** obtained from the elemental analysis method.¹³³ The IEC of the sulfonated poly(ether ether sulfone) derivative **SPSU-2** was calculated from the elemental analysis data as follows:^{134, 135}

IEC = 1000 Sc/ MWs

Where Sc : resultant sulphur content determined by elemental analysis, 0.82 %.

MWs : the molecular weight of sulphur, 32.1 g.

IEC : in mmol/g.

An IEC value of 0.25 mmol/g was obtained, in comparison with the ion exchange capacity value of 0.91 mmol/g for Nafion-117 as recorded by Luo and coworkers.¹⁶⁴

A new, well-defined sulfonated poly(ether ether sulfone) derivative **SPSU-2** has been prepared by the reaction of poly(ether ether sulfone) derivative **PSU-2** with sodium 3mercapto-1-propane sulfonate via the thiol-ene functionalization method. Spectroscopy data as well as TGA, DSC, XRD, TEM and AFM analyses confirm the regiospecific introduction of the alkyl sulfonate group along the polymer backbone. The new sulfonated poly(ether ether sulfone) derivative **SPSU-2** is thermally less stable than the poly(ether ether sulfone) precursor **PSU-2**, but exhibits a higher glass transition temperature due to the introduction of the pendant alkyl sulfonate group which reduces the polymer chain flexibility.

4.3 Synthesis of Poly(ether ether ketone)s based on Functionalized 1,1-Diphenylethylene Derivatives

Poly(ether ether ketone)s are a special class of engineering polymers with good chemical and physical stability, excellent mechanical properties and good hydrolytic stability. In general, poly(ether ether ketone)s are semicrystalline polymers with limited solubility in common organic solvents. The most efficient synthesis routes for the preparation of poly(ether ether ketone)s involves the following synthesis methods^{6, 7}:

- (a) The base catalyzed nucleophilic substitution polymerization reactions of dihalogenated diaryl ketones with bisphenols.^{6,7}
- (b) The electrophilic aromatic substitution reactions in step-growth polymerization.^{6,7}
- (c) The metal catalyzed coupling polymerization reactions of dihalogenated diaryl ketones with silylated bisphenols.^{6, 7}

In the present study, a series of new poly(ether ether ketone) derivatives was prepared by the cesium fluoride catalyzed polycondensation reactions of 4,4'-difluorobenzophenone (6) with different mole percentage ratios of silylated derivatives, 2,2-bis(4-*t*-butyldimethylsiloxy-phenyl)propane (2) and 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3) in N-methyl-2-pyrrolidone at 150 °C.

4.3.1 Synthesis and Purification of Monomers

4.3.1.1 Purification of 4,4'-Difluorobenzophenone (6)

Recrystallization of commercially available 4,4[']-difluorobenzophenone (6) from ethanol gave a pure product as white crystals with a melting point of 102 - 104 °C (lit mp¹³⁷ = 102 - 104 °C) and the following structure:



4.3.1.2 Synthesis of 2,2-Bis(4-*t*-butyldimethylsiloxyphenyl)propane (2)

The synthesis of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) from the reaction of bisphenol A with *t*-butyldimethylsilyl chloride and imidazole hydrochloride in methylene chloride has been reported in the literature.¹⁴⁸ A synthetic feature of the reaction is the facile removal of the imidazole salt by filtration. In addition, Quirk and coworkers¹³⁸ and De

Meulenaer and coworkers¹⁴⁰ outlined the synthesis of silylated bisphenol derivatives using different bisphenol compounds as starting material.

In the current study, the synthesis of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) was effected by the general procedure outlined by Quirk and Wang,¹³⁸ with modifications. The reaction of bisphenol A with *t*-butyldimethylsilyl chloride in the presence of imidazole and N,N-dimethylformamide gave the crude product as a clear viscous residue. Purification of the product by column chromatography using petroleum ether and ethyl acetate (80/20 = v/v) as eluent gave a clear viscous product. The viscous product solidified on standing to form a white solid, data which was previously not reported in the literature. Recrystallization of the white solid from absolute ethanol gave pure 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) as white crystals in 94 % yield and a melting point of 69 – 72 °C.

The following reaction pathway outlines the synthetic route for the preparation of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (2):



The structure of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) was confirmed by ¹H NMR (**Figure 1**) and ¹³C NMR (**Figure 2**) spectrometry and FTIR (**Figure 3**) analysis. A modified synthesis pathway for the preparation of the silylated bisphenol A derivative, 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) is reported. After purification of the product by column chromatography, a clear viscous product was isolated and solidified on standing to form a white solid. Recrystallization of the white solid from absolute ethanol gave pure 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) as white crystals with a melting point of 69 - 72 °C.

4.3.1.3 Synthesis of 1,1-Bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3)

Symmetrical disubstituted 1,1-diphenylethylene derivatives can be prepared via the following synthesis pathways: (a) the conversion of the appropriate benzophenone precursor to the corresponding carbinol intermediate, followed by the thermal or acid catalyzed dehydration of the intermediate carbinol to produce the corresponding disubstituted 1,1-diphenylethylene derivative;¹³² (b) the direct conversion of disubstituted benzophenones to the corresponding disubstituted 1,1-diphenylethylene derivatives by the Wittig reaction with phosphoryl ylides¹³⁸ or the Tebbe reagent;¹⁵¹ and (c) via the copper-catalyzed C-H addition of arenes with aryl acetylenes to produce the corresponding disubstituted 1,1-diphenylethylene

The preparation of 1,1-bis[4-(t-butyldimethylsiloxy)phenyl]ethylene (**3**) was first reported by Quirk and Wang¹³⁸ using the following method:

- (a) The reaction of 4,4´-dihydroxybenzophenone with *t*-butyldimethylsilyl chloride in the presence of imidazole and N,N-dimethylformamide to form the intermediate 4,4´-bis(*t*butyldimethylsiloxy)benzophenone derivative.¹³⁸
- (b) The conversion of 4,4'-bis(t-butyldimethylsiloxy)benzophenone to 1,1-bis(4-tbutyldimethylsiloxyphenyl)ethylene (3) via the Wittig reaction with phosphoryl ylides.¹³⁸

However, the intermediate product, 4,4⁻-bis(*t*-butyldimethylsiloxy)benzophenone, was only obtained as a clear viscous liquid. In addition, Hejaz and coworkers¹⁵³ isolated the intermediate product, 4,4⁻-bis(*t*-butyldimethylsiloxy)benzophenone as a solid, but no melting point data was recorded.

The current research work reports the high yield synthesis pathway for the preparation of pure 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) which was isolated as white crystals. The procedure outlined by Quirk and Wang,¹³⁸ with modifications, was adopted and the synthetic route involved the following steps:

- (a) The preparation of 4,4´-bis(*t*-butyldimethylsiloxy)benzophenone using
 4,4´-dihydroxybenzophenone as the starting material, and
- (b) The direct conversion of 4,4'-bis(t-butyldimethylsiloxy)benzophenone to
 1,1-bis[4-(t-butyldimethylsiloxy)phenyl]ethylene (3) via the classic Wittig reaction as outlined in the following reaction scheme:



Preparation of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone:

The intermediate product, 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone, which was obtained after treatment of 4,4'-dihydroxybenzophenone with *t*-butyldimethylsilyl chloride in the presence of imidazole in N,N-dimethylformamide for 3 hours, was purified by column chromatography to give 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone as a white solid. Recrystallization of the white solid from absolute ethanol gave pure 4,4⁻-bis(*t*-butyldimethylsiloxy)benzophenone as fine white crystals in 66 % yield with a melting point of 52.5 – 55.7 °C.

The structure of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone was confirmed by ¹H NMR spectrometry (**Figure 4**), ¹³C NMR spectrometry (**Figure 5**) as well as FTIR analyses (**Figure 6**) and the spectral data is in good agreement with the data reported by Quirk and Wang.¹³⁸ The modified synthesis route for the conversion of the 4,4'-dihydroxybenzophenone to 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone afford the pure product as fine white crystals with a melting point of 52.5 – 55.7 °C.

Preparation of 1,1-Bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3):

The direct conversion of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone to the desired product, 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) was effected by the classic Wittig reaction at 0 °C. The rapid treatment of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone with the phosphoryl ylide, generated *in situ* from the reaction of methyllithium with methyltriphenylphosphonium bromide, gave a clear viscous product which solidified on standing to give a white solid. Recrystallization of the resultant white solid from absolute ethanol gave the target molecule, 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) as white crystals in 63 % yield with a melting point of 55.9 - 56.4 °C (lit mp¹³⁸ = 56 - 57.5 °C). The structure of 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene, (**3**) was confirmed by ¹H NMR spectrometry (**Figure 7**), ¹³C NMR spectrometry (**Figure 8**) as well as FTIR analysis (**Figure 9**) and the spectroscopic data correspond well with the data reported by Quirk and Wang.¹³⁸

The synthesis of 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) was performed via a two step synthesis method using 4,4'-dihydroxybenzophenone as starting material. The high yield formation of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone as white crystals was effected by the reaction of 4,4'-dihydroxybenzophenone with *t*-butyldimethylsilyl chloride. The subsequent Wittig reaction of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone with an appropriate phosphoryl ylid afforded 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) as white crystals. Results show that the treatment of 4,4'-bis(*t*-bis(*t*-butyldimethylsiloxy)phenyl]ylid afforded 1,1-bis[4-(*t*-bis(*t*-b

benzophenone impurity.

4.3.2 Synthesis of Poly(ether ether ketone)s by Step-Growth Polymerization Methods

4.3.2.1 The Cesium Fluoride Catalyzed Polymerization of Dihalogenated Diaryl Ketones with Silylated Bisphenols

The synthesis of poly(ether ether ketone)s by step-growth polymerization using dihalogenated diaryl ketones and silylated bisphenols as monomers in the presence of cesium fluoride as catalyst was first reported by Kricheldorf and coworkers^{29, 30, 78, 79}. Similarly, a new series of poly(ether ether ketone)s were prepared by the cesium fluoride catalyzed coupling polymerization reactions of 4,4⁻-difluorobenzophenone (**6**) with different mole percentage ratios of silylated monomers, 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**) and

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1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) in NMP as solvent at 150 °C according to the following reaction scheme:



In a typical procedure, the synthesis of the poly(ether ether ketone) derivative, **PEEK-2** was effected by the polycondensation reaction of 4,4[']-difluorobenzophenone (**6**) and a specific mole percentage ratio of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**2**): 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (**3**) = 80:20 in the presence of cesium fluoride as the catalyst in NMP at 150 °C for 12 hours. The polymer product was precipitated into methanol,

filtered and vacuum dried to afford pure poly(ether ether ketone) derivative **PEEK-2** as a white solid.

The experimental data for the preparation of the different poly(ether ether ketone) derivatives is outlined in the following table:

Polymer	Monomer (6)	Monomer (2)	Monomer (3)
	mol %	mol %	mol %
PEEK-1	100	100	0
PEEK-2	100	80	20
PEEK-3	100	50	50
PEEK-4	100	20	80
PEEK-5	100	0	100

4.3.3. Characterization of the Different Poly(ether ether ketone)s Derivatives

To study the effect of the introduction of the 1,1-diphenylethylene unit along the polymer backbone, a series of new poly(ether ether ketone) derivatives was prepared by the cesium fluoride catalyzed step-growth polymerization of dihalogenated diaryl ketones with silylated bisphenols. The synthesis and characterization of poly(ether ether ketone) **PEEK-2** as a representative sample is discussed in detail and the characterization data compared with the different PEEK samples, where applicable. In a typical procedure, the synthesis of poly(ether ether ketone) **PEEK-2** was effected by the polycondensation reaction of 4,4′- difluorobenzophenone (6) with 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (2) and 1,1bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3) using cesium fluoride as the catalyst in NMP at 150 °C for 12 hours with the mole percentage ratio of the monomer feed of [6]:[2]:[3] = [100]:[80]:[20]. The resulting polymer was coagulated in methanol, filtered and vacuum dried to afford the poly(ether ether ketone) derivative **PEEK-2** as a white solid.

The molecular weight data of **PEEK-1** and **PEEK-2**, the only poly(ether ether ketone) derivatives completely soluble in tetrahydrofuran, were determined by size exclusion chromatography. The molecular weight characteristics of the THF insoluble poly(ether ether ketone) derivatives were determined by dilute solution viscometry analyses. The number average molecular weight, the molecular weight distribution data and the inherent viscosity data for different poly(ether ether ketone) derivatives as determined by size exclusion chromatography and dilute solution viscometry measurements, respectively are depicted in the following table:

Polymer	$\overline{\mathbf{M}}_{\mathbf{n}}$	$\overline{\mathbf{M}}_{\mathbf{w}}$	$\overline{\mathbf{M}}_{\mathbf{w}}/\overline{\mathbf{M}}_{\mathbf{n}}$	$\eta_{inh} \left(dL/g \right)$
	×10 ⁻³ g/mol	×10 ⁻³ g/mol		at 25 °C
PEEK-1	6.6	8.2	1.24	0.10
PEEK-2	6.9	8.3	1.20	0.12
PEEK-3	-	-	-	0.18
PEEK-4	-	-	-	0.29
PEEK-5	-	-	-	0.53

The size exclusion chromatogram (Figure 31) of the poly(ether ether ketone) derivative,

PEEK-2 shows a broad monomodal molecular weight distribution curve with $\overline{M}_n = 6.9 \times 10^3$ g/mol and $\overline{M}_w/\overline{M}_n = 1.20$. The size exclusion chromatography data shows that the number average molecular weight of the 1,1-diphenylethylene based poly(ether ether ketone) derivative, **PEEK-2** is higher than the number average molecular weight of poly(ether ether ketone) derivative, **PEEK-1**, indicating that the introduction of 20 mole percentage of 1,1-diphenylethylene moiety into the polymer backbone leads to an increase in the number average molecular weight of the resultant poly(ether ether ketone) derivative. The poly(ether ether ketone) derivatives **PEEK-3**, **PEEK-4** and **PEEK-5** are only slightly soluble in THF. Thus, the inherent viscosity data of each sample was determined by dilute solution viscometry measurements. The dilute solution viscometry data shows that the inherent viscosity values increase with increasing 1,1-diphenylethylene content in the polymer chain and inherent viscosity values in the range of 0.10 to 0.53 dL/g were obtained.

The ¹H NMR spectrum (**Figure 32**) of poly(ether ether ketone) derivative **PEEK-2** shows a singlet at $\delta = 1.71$ ppm, due to the resonance of the protons of the methyl groups of the isopropylidene unit of the bisphenol A moiety. The singlet at $\delta = 5.45$ ppm, which corresponds to the resonance of the protons of the C=CH₂ group, confirms the introduction of the 1,1-diphenylethylene unit along the polymer backbone. A multiplet between $\delta = 6.98$ - 7.81 ppm is attributed to the resonance of the aromatic protons of the different p-substituted benzene rings along the polymer backbone.

The ¹³C NMR spectrum (**Figure 33**) of the poly(ether ether ketone) derivative **PEEK-2**, shows a signal at $\delta = 114.81$ ppm, attributed to the resonance of the carbon atom of the C=<u>C</u>H₂ groups along the polymer backbone. The signal at $\delta = 194.28$ ppm is assigned to the resonance of the carbonyl carbon atoms along the polymer chain. The absence of any carbon atom resonance at -4.40 ppm and 25.69 ppm confirms the complete polymerization reaction and absence of any silylated monomer contaminant.

The FTIR spectrum (**Figure 34**) of poly(ether ether ketone) derivative **PEEK-2** shows an absorption band at 1654 cm⁻¹, attributed to the C=O stretching mode of the ketone groups along the polymer backbone. The absorption bands at 1497 and 1584 cm⁻¹ correspond to the C=C stretching modes of the aromatic phenyl rings.

The thermal stability of each poly(ether ether ketone) derivative was determined by thermogravimetric analysis. The TGA curve (**Figure 35**) of the poly(ether ether ketone) derivative **PEEK-2** shows a two step thermal degradation pattern: (a) a weight loss of 5.7 % was observed at 80 °C – 125 °C, due to the loss of residual solvent from the polymer, (b) rapid weight loss of 47 % between 457 °C and 700 °C, attributed to the degradation of the polymer backbone. The 1,1-diphenylethylene based poly(ether ether ketone) derivative **PEEK-5**, which contains the highest 1,1-diphenylethylene content, is thermally less stable than the bisphenol A based poly(ether ether ketone) **PEEK-1**, which indicates that the introduction of the 1,1-diphenylethylene unit decreases the thermal stability of the resultant poly(ether ether ketone) derivative. In addition, the weight percentage retained at 800 °C is higher for the

poly(ether ether ketone) derivatives with the higher 1,1-diphenylethylene content. The TGA data for each poly(ether ether ketone) derivative is outlined in the following table:

Polymer	T ₂₀ (°C)	T _d	W _{650°C} (%)
PEEK-1	529	459	52
PEEK-2	513	457	46
PEEK-3	512	447	44
PEEK-4	507	440	42
PEEK-5	445	435	34

where T_{20} represents the 20 % weight loss temperature, T_d represents the onset temperature for polymer chain decomposition and $W_{650^{\circ}C}$ represents the percentage weight loss at 650°C, the temperature at which complete polymer degradation is observed.

The glass transition temperature for each poly(ether ether ketone) sample was determined by differential scanning calorimetry and the T_g values are shown in the following table:

Polymer	$T_{g}(^{\circ}C)$
PEEK-1	121
PEEK-2	123
PEEK-3	130
PEEK-4	133
PEEK-5	135

The DSC thermogram of the poly(ether ether ketone) derivative **PEEK-2** is shown in **Figure 36**. A glass transition temperature of $T_g = 123$ °C was recorded for the poly(ether ether ketone) derivative **PEEK-2**. Results show that the introduction of 20 mole percentage of the 1,1-diphenylethylene unit into the polymer backbone increases the T_g value when compared to the T_g value of the corresponding bisphenol A based poly(ether ether ketone) **PEEK-1**. Furthermore, the T_g of the 1,1-diphenylethylene based poly(ether ether ketone) **PEEK-5** ($T_g =$ 135 °C) is significantly higher than the corresponding bisphenol A based poly(ether ether ketone), **PEEK-1** ($T_g = 121$ °C). The T_g data shows that the introduction of the non-planar, rigid 1,1-diphenylethylene unit increases the polymer chain stiffness and reduces the polymer chain mobility and subsequently higher T_g values were obtained for polymers with increased 1,1-diphenylethylene content.

The membrane characteristics of the different poly(ether ether ketone) derivatives were evaluated by AFM analysis. A dense membrane of the poly(ether ether ketone) derivative **PEEK-2** was prepared by spin coating an NMP solution of the polymer onto a glass plate to give the dense membrane before the AFM analysis. The AFM image of the poly(ether ether ketone) derivative **PEEK-2** is shown in **Figure 37.** The AFM image of the dense membrane of the poly(ether ether ketone) derivative **PEEK-2** is shown in **Figure 37.** The AFM image of the dense membrane of the poly(ether ether ketone) derivative **PEEK-2** displays dark regions which represents pores of different shapes and sizes varying between 0.1 and 0.25 μ m. The lighter regions or nodule groups correspond to spherical polymer aggregates with nodule sizes varying between 123 – 744 nm. The membrane is not smooth, but displays a relatively high surface roughness value of 9.74 nm.

The morphology of each poly(ether ether ketone) derivative in the powder form was evaluated by transmission electron microscopy. The TEM micrograph (**Figure 38**) of poly(ether ether ketone) derivative **PEEK-2** depicts spherical polymeric plate structures of different sizes and shapes.

The X-ray diffraction patterns for the different poly(ether ether ketone) derivatives in the powder form were recorded in order to determine the degree of crystallinity of each polymer sample. The X-ray diffraction pattern (**Figure 39**) of the poly(ether ether ketone) derivative **PEEK-2** shows characteristic broad peaks between $2\theta = 10 - 25^{\circ}$ and $28 - 50^{\circ}$ which correspond with the amorphous and crystalline regions, respectively, which is typical of semi-crystalline polymers.¹⁶¹⁻¹⁶³

Elemental analysis of the poly(ether ether ketone) derivative **PEEK-2** was determined by elemental analysis and gave the following data:

Elemental analysis (calculated): C, 82.79; H, 5.61.

Elemental analysis (found) : C, 54.89; H, 3.65

In addition, the elemental composition of the poly(ether ether ketone) derivative **PEEK-2** was determined by energy dispersive spectroscopy (EDS) measurements. The EDS data for the poly(ether ether ketone) derivative **PEEK-2** are depicted in the following table and show that elemental sulphur was not present in the poly(ether ether ketone) derivative **PEEK-2**:

Element	Elements Weight %	Weight % error	Atom %
СК	9.89	0.24	14.77
OK	56.13	-	62.92
NaK	7.40	0.13	5.77
MgK	1.35	0.10	1.00
AlK	0.66	0.05	0.44
SiK	21.56	0.14	13.74
CaK	31.05	0.06	1.36
Total	100		100

A series of new, well-defined poly(ether ether ketone) derivatives was prepared by catalytic arylation polycondensation reactions between dihalogenated diaryl ketones and silylated bisphenols. The different semicrystalline polymers were characterized by ¹H NMR spectrometry, ¹³C NMR spectrometry and FTIR spectroscopy and confirms the regiospecific introduction of the 1,1-diphenylethylene along the polymer backbone. In addition, the 1,1-diphenylethylene based poly(ether ether ketone) derivatives are thermally less stable than the bisphenol A based poly(ether ether ketone) derivatives, but the T_g values of the resultant polymers increases with increased 1,1-diphenylethylene content. The membrane characteristics and polymer morphology of the poly(ether ether ketone) derivatives were evaluated by AFM and TEM analyses, respectively and show good membrane integrity and stability.

4.4 Synthesis and Characterization of Sulfonated Poly(ether ether ketone)s

Several post-polymerization sulfonation routes for the introduction of the sulfonic acid group onto the poly(ether ether ketone) backbone have been reported in the literature.^{37, 94-100} However, such sulfonation reactions proceed without the control of the amounts and the position of sulfonate groups along the poymer backbone. Recently, thiol-ene click chemistry methods for the post-polymerization functionalization of different polymer backbones were developed by the late Charles Hoyle and coworkers.⁶¹ Subsequently, Guan and coworkers ¹⁵ prepared sulfonated poly(ether ether ketone) via the thiol-ene free radical coupling reaction of the parent poly(ether ether ketone), substituted with the pendant propenyl functional group, using sodium 3-mercapto-1-propane sulfonate as the sulfonating agent in the presence of AIBN. Similarly, due to the regiospecific introduction of the $C=CH_2$ group along the polymer backbone of the different poly(ether ether ketone) derivatives (PEEK-2 to PEEK-5), a new sulfonation method using thiol-ene chemistry was developed for the synthesis of sulfonated poly(ether ether ketone) derivatives using the new poly(ether ether ketone) samples as precursors. In the present study, a new sulfonated poly(ether ether ketone) derivative was prepared from the reaction of poly(ether ether ketone) derivative **PEEK-2** with sodium 3mercapto-1-propane sulfonate in the presence of AIBN as initiator in NMP/DMSO at 75 °C for 5 days. The polymer product was purified by dialysis with 30 % aqueous acetone for 72 hours. The polymer product was precipitated into water, filtered and vacuum dried to afford sulfonated poly(ether ether ketone) **SPEEK-2** as a white solid. The reaction scheme for the sulfonation of poly(ether ether ketone) derivative **PEEK-2** via the thiol-ene reaction is depicted as follows:



The sulfonation reaction using the thiol-ene click chemistry method is regiospecific since the reaction occurs between the 1,1-diphenylethylene unit along the polymer backbone and the sulfonating agent, sodium 3-mercapto-1-propane sulfonate and results in the formation of a sulfonated polymer with controlled degree of sulfonation. The size exclusion chromatogram (**Figure 40**) of sulfonated poly(ether ether ketone) **SPEEK-2** shows a monomodal molecular weight distribution curve with $\overline{M}_n = 7.1 \times 10^3$ g/mol and molecular weight distribution of 1.21.

The ¹H NMR spectrum (**Figure 41**) of the sulfonated poly(ether ether ketone) derivative **SPEEK-2**, shows the following characteristic peaks:^{15, 69, 70, 132} (a) a singlet at $\delta = 1.65$ ppm, due to the resonance of the protons of the methyl groups from the bisphenol A moeity; (b) a quintet at $\delta = 1.84 - 1.92$ ppm, ascribed to the resonance of the methylene protons of the alkyl sulfonate group, CH₂-CH₂-CH₂SO₃Na; (c) a triplet at $\delta = 2.15 - 2.20$ ppm, due to the resonance of the methylene protons of the S-CH₂-CH₂-CH₂SO₃Na group; (d) a triplet at $\delta = 2.67 - 2.75$ ppm, assigned to the resonance of the protons of the (CH₂)₂-CH₂-SO₃Na group. The triplet at $\delta = 4.37 - 4.41$ ppm and the doublet at $\delta = 4.45 - 4.47$ ppm, due to the resonances of the methine proton of R₂-C<u>H</u>-CH₂ and the protons of R₂CH-C<u>H</u>₂-S respectively, which indicates that the thiol-ene reaction between the sulfonating agent and the diphenylethylene unit along the polymer backbone proceeded via the anti-Markovnikov addition method.¹⁵

The ¹³C NMR spectrum (**Figure 42**) of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** shows characteristic peaks at $\delta = 30.59$ ppm (S-<u>C</u>H₂-CH₂-CH₂SO₃Na), $\delta = 31.19$ ppm (C-(<u>C</u>H₃)₂), $\delta = 42.40$ ppm (<u>C</u>-(CH₃)₂) and $\delta = 63.56$ ppm (<u>C</u>H-CH₂-S-CH₂) which confirms the introduction of the sulfonating unit pendant to the polymer backbone.

The FTIR spectrum (**Figure 43**) of the sulfonated poly(ether ether ketone) **SPEEK-2** displays an absorption band at 1657 cm⁻¹, due to the C=O carbonyl stretching modes of the ketone groups along the polymer backbone. The absorption bands at 1024, 1496 and 1590 cm⁻¹ are attributed to the O=S=O stretching modes of the sulfonate groups and the C=C vibration and stretching modes of the aromatic rings along the polymer backbone, respectively.

The thermal stability of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** was determined by thermogravimetric analysis. The TGA thermogram (**Figure 44**) of sulfonated poly(ether ether ketone) derivative **SPEEK-2** exhibits a three phase thermal degradation pattern: (a) a weight loss of 0.43 % between 100 - 125 °C, attributed to the loss of moisture and residual solvent within the polymer; (b) a weight loss of 1.9 % between 310 – 350 °C, due to the thermal decomposition of the pendant alkyl sulfonate groups; and (c) a rapid weight loss

of 47 % between 500 – 600 °C, which corresponds to the degradation of the polymer backbone. Due to the introduction of the pendant alkyl sulfonate groups, the sulfonated poly(ether ether ketone) derivative **SPEEK-2** is thermally less stable than the poly(ether ether ketone) precursor **PEEK-2** between 100 – 600 °C, but the mass retained after 800 °C is higher for the sulfonated poly(ether ether ketone) **SPEEK-2**.

The glass transition temperature of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** was determined by differential scanning calorimetry. The DSC thermogram (**Figure 45**) for sulfonated poly(ether ether ketone) derivative **SPEEK-2** shows a glass transition temperature of 148 °C. The T_g value for the sulfonated poly(ether ether ketone) derivative **SPEEK-2** is higher than the T_g value of poly(ether ether ketone) **PEEK-2** (T_g = 123 °C) due to the introduction of pendant alkyl sulfonate groups to the polymer backbone. The pendant alkyl groups as well as the interchain association of the sulfonate groups reduce the chain flexibility and consequently increases the T_g of the sulfonated poly(ether ether ketone) **SPEEK-2**. The DSC data shows that the sulfonated poly(ether ether ketone) derivative **SPEEK-2** is amorphous with no melting peak or crystallization peak detected up to 400 °C.

Atomic force microscopy was used to determine the morphology and membrane characteristics of sulfonated poly(ether ether ketone) derivative **SPEEK-2**. A dense membrane from sulfonated poly(ether ether ketone) was prepared by the spin coating method for AFM analysis. The AFM image (**Figure 46**) of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** displays dark domains which are attributed to pores with different sizes and shapes and pore sizes between 297 – 563 nm. The light circular and spherical regions

correspond to the nodules or polymer aggregates within the polymer membrane. The surface of the membrane shows a surface roughness value of 2.4 nm, indicating that the sulfonation reaction produced a smoother membrane when compared to the membrane obtained from the poly(ether ether ketone) **PEEK-2** precursor.¹⁵⁵⁻¹⁵⁷

The morphology of sulfonated poly(ether ether ketone) derivative **SPEEK-2** in the powder form was evaluated by transmission electron microscopy. Spherical aggregates of polymer consisting of lamellae of different sizes and shapes are observed as dark regions in the TEM image (**Figure 47**) of the sulfonated poly(ether ether ketone) derivative **SPEEK-2**.

The degree of crystallinity of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** in the powder form was determined by X–ray diffraction methods. The XRD pattern of sulfonated poly(ether ether ketone) derivative **SPEEK-2** is shown in **Figure 48** and indicates that the polymer structure is predominantly amorphous. A broad peak between $2\theta = 20^{\circ} - 25^{\circ}$ confirmed the predominant amorphous character of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** which is attributed to the presence of alkyl sulfonate groups along the polymer backbone of the sulfonated polymer.

The percentage sulphur content of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** was determined by elemental analysis and gave the following data:

Elemental analysis (calculated): C, 71.9; H, 5.31; Na, 2.29; O, 14.33; S, 6.38. Elemental analysis (found) : C, 21.96; H, 1.72; S, 0.22. In addition, the elemental composition of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** was determined by energy dispersive spectroscopy (EDS) measurements. The EDS data for the sulfonated poly(ether ether ketone) derivative **SPEEK-2** is depicted in the following table:

Element	Elements Weight %	Weight % error	Atom %
СК	25.77	0.20	31.96
ОК	71.17	-	66.27
FK	-	-	-
NaK	1.46	0.06	0.95
SiK	1.09	0.03	0.58
SK	0.52	0.03	0.24
Total	100		100

The EDS data of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** show the presence of elemental sulphur, which confirms the introduction of the mercaptopropyl sulfonate group pendant to the polymer. The sulfur content of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** of 0.24 atom percent of sulphur in the polymer backbone was obtained by EDS measurements.

The ion exchange capacity of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** was calculated from the percentage of sulphur content obtained from EDS data and elemental

analysis. For the sulfonated poly(ether ether ketone) derivative **SPEEK-2**, the sulphur content obtained by elemental analysis is 0.22 %. The IEC value was calculated as follows:^{134, 135}

IEC = 1000 Sc/ MWs

Where Sc : sulphur content determined by elemental analysis, 0.22 %.

- MWs : the molecular weight of sulphur, 32.1 g.
- IEC : in mmol/g.

An IEC value of 0.07 mmol/g was obtained for the sulfonated poly(ether ether ketone) derivative **SPEEK**^{134, 135} and compared favourably with the average IEC value of 0.91 mmol/g for Nafion-117 with higher degree of sulfonation.¹⁶⁴

The synthesis of a new sulfonated poly(ether ether ketone) derivative **SPEEK-2** via a new sulfonation post-polymerization method is described. The sulfonation reaction involves the treatment of 1,1-diphenylethylene based poly(ether ether ketone) **PEEK-2** with sodium 3-mercapto-1-propane sulfonate via the classic thiol-ene functionalization method to effect the regiospecific introduction of the alkyl sulfonate groups pendant to the polymer chain. The structure of the sulfonated poly(ether ether ketone) derivative **SPEEK-2** was confirmed by SEC, ¹H NMR and ¹³C NMR spectrometry as well as FTIR analysis. TGA and DSC data show that the sulfonated poly(ether ether ketone) derivative **SPEEK-2** is thermally less stable, but exhibits a higher Tg value when compared to the poly(ether ether ketone) precursor **PEEK-2**. AFM and TEM data show that membranes obtained from the sulfonated poly(ether ether ketone) derivative specific from the sulfonated poly(ether ether ketone) derivative specific the sulfonated poly(ether ether ketone) derivative specific is thermally less stable, but exhibits a higher Tg value when compared to the poly(ether ether ketone) precursor **PEEK-2**. AFM and TEM data show that membranes obtained from the sulfonated poly(ether ether ketone) derivative specific specif

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sulfonated poly(ether ether ketone) derivative **SPEEK-2** with low levels of sulfonation compares favourably to Nafion-117 with higher degree of sulfonation.

4.5 Synthesis of Polyimides based on Functionalized 1,1-Diphenylethylene Derivatives

Polyimides are thermally stable engineering polymers used as dielectric and packing material in the microelectronics industry. The high thermal stability, chemical inertness and good adhesion make polyimides the material of choice for applications in the semi-conductor industry. In addition, polyimides are extensively used in the manufacture of optical films, aircraft and automobile engines as well as membranes in fuel cell technology.¹⁶⁵⁻¹⁶⁶

In general, polyimides can be prepared via three different synthetic methods, namely:

- (a) The one step melt polymerization of diamines with tetracids or diacids/diesters.¹⁶⁵⁻¹⁶⁶
- (b) The two step polycondensation reaction between aromatic tetracarboxylic dianhydrides and aromatic diamines at room temperature in a polar aprotic solvent.¹⁶⁵⁻¹⁶⁶ In the first step, the polycondensation reaction between an aromatic tetracarboxylic dianhydride and an aromatic diamine proceeds via a ring-opening polyaddition reaction to form the polyamic acid intermediate. In the second step, the polyamic acid intermediate undergoes a thermal or chemical imidization reaction to produce the corresponding polyimide.
- (c) A three step polymerization process which involves the formation of polyisoimides as intermediate polymer products.¹⁶⁵⁻¹⁶⁶

Most polyimides in the fully cyclised state cannot be processed due to their high glass transition temperature and insolubility in common organic solvents. To improve the processability of aromatic polyimides, it is common to introduce a flexible monomeric unit into the polymer repeating unit directly or by post-polymerization functionalization reactions. In the present study, a series of new aromatic polyimide derivatives were prepared by step-growth polymerization methods by the polycondensation reactions of 4,4′-oxydiphthalic anhydride (**7**) with different mole percentage ratios of 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**8**) and 1,1-bis(4-aminophenyl)ethylene (**9**) as monomer precursors. The intermediate polyamic acids were subjected to a thermal imidization process to provide the corresponding polyimide derivatives.

4.5.1 Synthesis and Purification of Monomers

4.5.1.1 Purification of 4,4'-Oxydiphthalic Anhydride (7)

Recrystallization of commercially available 4,4⁻-oxydiphthalic anhydride (**7**) from acetic anhydride gave a pure product as white crystals with a melting point of 224 – 226 °C (lit mp¹⁴³ = 224 – 226 °C) and the following structure:



(7)

4.5.1.2 Purification of 2,2-Bis[4-(4-aminophenoxy)phenyl]propane (8)

The commercially available 2,2-bis[4-(4-aminophenoxy)phenyl]propane (8) was purified by recrystallization from ethanol, vacuum dried at 60 °C for 12 hours to afford pure product as white crystals with a melting point of 127 - 130 °C (lit mp¹⁴⁴ = 129 °C) and the following structure:



(8)

4.5.1.3 Synthesis of 1,1-Bis(4-aminophenyl)ethylene (9)

The preparation of symmetrical diamine functionalized 1,1-diphenylethylene derivatives can be accomplished by different synthetic organic chemistry methods.¹⁴⁶ Bencze¹⁴⁷ reported a method for the synthesis of 1,1-bis(4-aminophenyl)ethylene (**9**) by the reaction of 3,3-di(4-aminophenyl)-2-butanone with phosphoric acid. In addition, the high yield preparation of 1,1-bis(4-aminophenyl)ethylene (**9**) by the Friedel-Craft reaction of the aromatic substrates with 1,1,1-trichloroethane was reported by Sonawane and coworkers.¹⁵³ Recently, Ndawini¹⁴⁶ reported the preparation of 1,1-bis(4-aminophenyl)ethylene (**9**) by a new method which involves the Wittig reaction using 4,4´-diaminobenzophenone as substrate. In the present study, the preparation of 1,1-bis(4-aminophenyl)ethylene (**9**) was effected by the Wittig reaction using 4,4'-diaminobenzophenone as starting material as outlined by Ndawuni.¹⁴⁶ Treatment of 4,4'-diaminobenzophenone with a phosphorous ylide, generated *in situ* from the reaction of methyllithium and methyltriphenylphosphonium bromide, in dry tetrahydrofuran under reflux for 12 hours gave 1,1-bis(4-aminophenyl)ethylene (**9**) according to the following reaction pathway:



Column chromatography of the crude product using petroleum ether/ethyl acetate (50/50 = v/v) as eluent afforded a pale yellow solid. Recrystallization of the crude product from ethanol/water = 80/20 afforded 1,1-bis(4-aminophenyl)ethylene (9) as yellow crystals in 52 % yield and a melting point of 161.5 – 163.1 °C (lit mp¹⁴⁷ = 170 – 172 °C).
The ¹H NMR spectrum (**Figure 49**) of 1,1-bis(4-aminophenyl)ethylene (**9**) exhibits the following spectral characteristics: (a) a broad singlet at $\delta = 3.69$ ppm, attributed to the resonance of the primary amine protons of the NH₂ groups; (b) a singlet at $\delta = 5.19$ ppm, due to the resonance of the equivalent methylene protons of the C=CH₂ group; and (c) a doublet of doublets at $\delta = 6.61 - 7.25$ ppm, which correspond to the resonance of the aromatic protons of the p-substituted benzene rings.

The ¹³C NMR spectrum (**Figure 50**) of 1,1-bis(4-aminophenyl)ethylene (**9**) shows a peak at δ = 109.71 ppm, attributed to the resonance of the olefin carbon atom of the terminal C=CH₂ and a signal at 132.31 ppm, due to the resonance of the C-2 carbon of the CH₂=CR₂ group, consistent with literature reports.¹³⁸

The FTIR spectrum (**Figure 51**) of 1,1-bis(4-aminophenyl)ethylene (**9**) shows the presence of absorption bands at 3435 cm⁻¹ and 890 cm⁻¹, due to the stretching modes of the N-H and the =C-H (of C=CH₂) bonds, respectively.

A synthesis route for the conversion of 4,4⁻-diaminobenzophenone to 1,1-bis(4aminophenyl)ethylene (**9**) by the classic Wittig reaction gave the pure product as yellow crystals in 52 % yield with a melting point of 161.5 - 163.1 °C. The structure was confirmed by ¹H NMR and ¹³C NMR spectrometry and FTIR analysis and the spectroscopic data is consistent with the data reported by Ndawuni.¹⁴⁶

4.5.2 Synthesis of Polyimides by Step-Growth Polymerization Methods

4.5.2.1 The Polymerization of Aromatic Tetracarboxylic Dianhydrides with Aromatic Diamines followed by a Thermal Imidization Process

The synthesis of aromatic polyimides by a two step polycondensation reaction using aromatic dianhydrides and aromatic diamines as monomer precursors is the most efficient method for the preparation of aromatic polyimides. In general, aromatic polyimides cannot be processed due to their high T_g values and low solubility in organic solvents. The processability of aromatic polyimides can be overcome by processing the intermediate polyamic acid derivatives, followed by the formation of the polyimide via a thermal imidization process. In the current study, a new series of polyimide derivatives were prepared by step-growth polymerization of 4,4'-oxydiphthalic anhydride (**7**) with different mole percentage ratios of 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**8**) and 1,1-bis(4-aminophenyl)ethylene (**9**) in N,N-dimethylacetamide as solvent according to the following pathway:



In a typical procedure, the preparation of the polyimide derivative **PI-2** was effected by the polycondensation reaction of 4,4'-oxydiphthalic anhydride (**7**) with a mole percentage ratio of 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**8**) : 1,1-bis(4-aminophenyl)ethylene (**9**) = 80:20 in N,N-dimethylacetamide at 30 °C for 24 hours. The step-growth polymerization reaction proceeded smoothly at 30 °C for 24 hours to afford the intermediate homogeneous polyamic acid solution. The polyamic acid solution was cast onto a glass plate and subjected to a thermal imidization process which involves heating the sample for an hour each at 100 °C, 200 °C and 250 °C. After removal of the film from the glass plate, the polyimide derivative **PI-2** was isolated as a brown film. The following table outlines the stoichiometry for the different polymerization reactions for the preparation of new polyimide derivatives:

Polymer	Monomer (7)	Monomer (8)	Monomer (9)
	mol %	mol %	mol %
PI-1	100	100	-
PI-2	100	80	20
PI-3	100	50	50
PI-4	100	20	80
PI-5	100	-	100

4.5.3 Characterization of the Different Polyimide Derivatives

A series of new polyimide derivatives were prepared by the step-growth polymerization method which involves the polycondensation of aromatic dianhydrides with aromatic

diamines, followed by a thermal imidization process. Polyimide derivatives with different 1,1-diphenylethylene content were prepared to determine the impact of the 1,1-diphenylethylene unit along the polymer backbone on polymer properties. In a typical procedure, the synthesis of the polyimide derivative **PI-2** was effected by the polycondensation reaction of 4,4'-oxydiphthalic anhydride (7) with 2,2-bis[4-(4aminophenoxy)phenyl]propane (8) and 1,1-bis(4-aminophenyl)ethylene (9) in DMAc for 24 hours with the mole percentage ratio of the monomer feed of [7]:[8]:[9] = [100]:[80]:[20] to provide the corresponding polyamic acid intermediate. In the second step, the thermal imidization of the polyamic acid derivative afforded the polyimide copolymer **PI-2** as a brown film. The synthesis and characterization data of polyimide **PI-2** as a representative sample are reported in detail and the data compared with the other polyimide samples, where applicable. The different polyimide derivatives are insoluble in common organic solvents such as THF. Thus, the molecular weight measurements for the different polyimide derivatives were obtained by dilute solution viscometry analyses. The inherent viscosity of the polyimide samples were determined using an Ubbelohde viscometer using sulfuric acid (98 %) solution as solvent. Inherent viscosity values in the range of 0.10 - 0.35 dL/g for the different polyimide derivatives were obtained, indicating the formation of low molecular weight polymers. The inherent viscosity of the polyimide derivative **PI-1** is lower than the 1,1diphenyethylene based polyimide derivative **PI-5**. In addition, inherent viscosity data shows that the molecular weight of the resultant polyimide derivatives increases with increasing 1,1diphenylethylene content. The inherent viscosity (n_{inh}) data of the different polyimides derivatives are listed in the following table:

Polymer	η _{inh} (dL/g)
	at 25 °C
PI-1	0.10
PI-2	0.24
PI-3	0.32
PI-4	0.35
PI-5	0.35

The ¹H NMR spectrum (**Figure 52**) of the polymide derivative **PI-2** shows the following spectral characteristics: (a) a singlet at $\delta = 1.65$ ppm, corresponding to the resonance of the protons of the methyl groups of the isopropylidene group of the monomer; (b) a singlet at $\delta = 5.65$ ppm, due to the resonance of the protons of the C=CH₂ of the 1,1-diphenylethylene unit moiety along the polymer backbone; and (c) a mutiplet at $\delta = 6.99 - 8.10$ ppm, due to the resonance of the protons of the phenyl rings along the polymer backbone.

The ¹³C NMR spectrum (**Figure 53**) of the polyimide derivative **PI-2** shows the following spectral data : (a) signals at $\delta = 31.14$ ppm and 42.28 ppm, assigned to the resonance of the primary and quaternary carbon atoms of the isopropylidene group of the monomer unit; (b) signals at $\delta = 114.19$ ppm and 134.98 ppm, corresponding to the resonance of the carbon atoms of C-1 (<u>CH</u>₂=CR₂) and C-2 (CH₂=<u>C</u>R₂) olefin carbon atoms of the CH₂= CR₂ group, respectively, confirming the incorporation of the 1,1-diphenylethylene moiety along the polymer backbone.

The FTIR spectrum (**Figure 54**) of the polyimide derivative **PI-2** displays absorption bands at 1779 cm⁻¹ and 1720 cm⁻¹, which are attributed to the stretching modes of the carbonyl groups of the imide functionality along the polyimide backbone. The absorption band at 730 cm⁻¹ is due to the C-N stretching vibrations of the imide groups along the polymer backbone.

The thermal characteristics of each polyimide derivative were determined by thermogravimetric analysis and differential scanning calorimetry. The TGA thermogram (**Figure 55**) of the polyimide derivative **PI-2** shows a two step degradation pattern with the following characteristics: (a) a weight loss of 0.7 % is observed between 100 °C – 150 °C, attributed to the loss of water and residual solvent in the polymer backbone; (b) a rapid weight loss of 47 % between 500 °C - 650 °C due to the degradation of the polymer backbone. As for the polyimide derivative **PI-5**, the TGA thermogram (**Figure 55**) shows a three step degradation pattern with the following characteristics: (a) a weight loss of 1.6 % is observed between 100 °C – 150 °C corresponding to the loss of water and residual solvent; (b) a weight loss of 15 % between 335 °C – 425 °C probably due to the degradation of the diphenylethylene portion of the polymer; (c) a weight loss of 23 % between 500 °C – 650 °C due to the degradation of the rest of the polymer matrix. The TGA analysis for each polyimide derivative is described in the following table:

Polymer	T ₁₀ (°C)	T _d	W _{650°C} (%)
PI-1	524	467	48
PI-2	523	456	47
PI-3	484	371	46
PI-4	441	337	43
PI-5	412	335	41

where T_{10} represents the 10 % weight loss temperature, T_d is the onset temperature for polymer chain decomposition and $W_{650^\circ C}$ represents the percentage weight loss at 650°C, the temperature at which complete polymer degradation is observed.

The DSC curve of the polyimide derivative **PI-2** is shown in **Figure 56**. A glass transition temperature of $T_g = 228$ °C was recorded for the polyimide derivative **PI-2**. The glass transition temperature of each polyimide derivative was determined by DSC and is shown in the following table:

Polymer	$T_{g}(^{\circ}C)$
PI-1	225
PI-2	228
PI-3	235
PI-4	239
PI-5	256

Data shows that the T_g values of the different polyimide derivatives range between 225°C - 256 °C and increases with the increased content of the 1,1-diphenylethylene unit. The introduction of 20 mole % of the 1,1-diphenylethylene unit increases the T_g value of polyimide derivative **PI-2** ($T_g = 228$ °C) when compared to the T_g value of the corresponding polyimide derivative **PI-1** (Tg = 225 °C). The increased polymer chain stiffness, due to the increased content of the rigid 1,1-diphenylethylene unit, coupled with the reduction in mole percentage ratio of the flexible isopropylidene unit and -O- groups, accounts for the higher T_g value for the 1,1-diphenylethylene based polyimide derivative **PI-2** when compared to polyimide derivative **PI-1**.

The membrane properties of the dense membrane of each polyimide derivative were determined atomic force microscopy analyses. The AFM image of the polyimide derivative **PI-2** is shown in **Figure 57**. The AFM image of the polyimide derivative **PI-2** shows light regions, high peaks and bright areas which is attributed to polymer nodules of different shapes and sizes. The darker regions in the AFM image represent pores of different pore sizes ranging between 54.7 - 150 nm.¹⁵⁵⁻¹⁵⁷ The AFM image depicts high surface roughness with surface roughness value of 7.96 nm for the polyimide derivative **PI-2**.

The morphology of the dense membrane of each polyimide derivative was investigated by transmission electron microscopy analysis. The TEM micrograph (**Figure 58**) of the polyimide derivative **PI-2**, in the powder form, shows an aggregate mass of spherical polymer materials. The TEM image of the cross-section of the dense membrane of the polyimide derivative **PI-2** exhibits a dark porous surface.

The X-ray diffraction patterns for the different polyimide derivatives in the film form were recorded to determine the degree of crystallinity of each polymer sample. The X-ray diffraction pattern (**Figure 59**) of the polyimide derivative **PI-2** shows that the sample is predominantly amorphous in nature with crystalline domains. The broad peaks between $2\theta = 20^{\circ} - 25^{\circ}$ is characteristic of the degree of amorphous character of the polymer sample. The sharp peaks between $2\theta = 30^{\circ}$ to 45° represent crystalline domains within the polymer sample.

Elemental analysis of the polyimide derivative **PI-2** was determined by elemental analysis and gave the following data:

Elemental analysis (calculated): C, 75.12; H, 4.20; N, 4.67; O, 16.01.

Elemental analysis (found) : C, 26.06; H, 1.02.

A series of new, well-defined polyimide derivatives was prepared by the two step polycondensation reactions between an aromatic tetracarboxylic dianhydride and different aromatic diamines. The intermediate polyamic acid derivatives were subject to a thermal imidization process to produce the corresponding polyimides. The different polyimide derivatives were characterized by ¹H NMR and ¹³C NMR spectrometry and FTIR spectroscopy and confirms the regiospecific introduction of the 1,1-diphenylethylene along the polymer backbone. Thermal analyses data of the different polyimide derivatives show that the thermal stability of a particular polyimide derivative decreases with increased 1,1diphenyethylene content, but the T_g value increases with increased 1,1-diphenyethylene

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content. AFM and TEM analyses show excellent membrane morphology data for the different polyimide derivatives.

4.6 Synthesis and Characterization of Sulfonated Polyimides

In general, sulfonated polyimides can be prepared via the direct copolymerization of sulfonated monomers or via direct post-polymerization sulfonation reactions using the intermediate polyamic acid or the polyimide as precursors.¹²⁶⁻¹²⁸ The thiol-ene reaction, which was developed by the late Charles Hoyle and his coworkers, has been extensively applied as a general post-polymerization functionalization reaction to afford a plethora of functionalized polymers with well-defined polymer properties.⁶³⁻⁶⁴ Subsequently, the synthesis of sulfonated poly(ether ether ketone) by the thiol-ene reaction was reported by Guan and coworkers.¹⁵ In the present study, a new sulfonated polyimide derivative **SPI-2** was prepared by the reaction of polyimide **PI-2** with sodium 3-mercapto-1-propane sulfonate and AIBN in NMP/DMSO at 75 °C for 5 days. The polymer product was subjected to a dialysis process with 30 % aqueous acetone for 3 days. The sulfonated polyimide **SPI-2** was isolated by precipitation into water, filtered and vacuum dried at 80 °C to give the sulfonated polyimide derivative **SPI-2** with solid. The following scheme outlines the synthesis of sulfonated polyimide **SPI-2** via the thiol-ene method:



The sulfonated polyimide derivative **SPI-2** is slightly soluble in THF. Thus, the molecular weight of sulfonated polyimide **SPI-2** was determined by dilute solution viscometry analysis using an Ubbelohde viscometer and sulfuric acid (98 %) as solvent and an inherent viscosity value of 0.25 dL/g at 25 °C was obtained. The inherent viscosity of the sulfonated polyimide **SPI-2** is almost the same as the inherent viscosity of the precursor polyimide derivative **PI-2**.

The ¹H NMR spectrum (**Figure 60**) of the sulfonated polyimide derivative **SPI-2** shows a singlet at $\delta = 1.64$ ppm, corresponding to the resonance of the protons of the methyl groups from the 2,2-bis[4-(4-aminophenoxy)phenyl]propane unit of the monomer precursor. In addition, the ¹H NMR spectrum exhibits the following peaks associated with the alkylsulfonate groups pendant to the polymer backbone of the sulfonated polyimide derivative **SPI-2**:^{15, 69, 70, 132} (a) a quintet at $\delta = 1.87 - 1.92$ ppm, due to the presence of the pendant –CH₂-CH₂-CH₂SO₃Na group along the polymer backbone; (b) a triplet at $\delta = 2.15 - 2.20$ ppm, attributed to the resonance of the methylene protons of the S-CH₂-CH₂SO₃Na group; (c) a triplet at $\delta = 2.64 - 2.72$ ppm, assigned to the resonance of the protons of the S-(CH₂)₂-CH₂-CH₂SO₃Na group; (d) a triplet at $\delta = 4.44 - 4.48$ ppm, due to the resonance of the methine proton

of R₂-C<u>H</u>-CH₂-S group; and (e) a doublet at $\delta = 4.50 - 4.52$ ppm, due to the resonance of the protons of the R₂-CH-C<u>H₂-S-</u> group.

The ¹³C NMR spectrum (**Figure 61**) of the sulfonated polyimide derivative **SPI-2**, shows peaks at $\delta = 31.40$ ppm (C(<u>CH</u>₃)₂), $\delta = 42.28$ ppm (<u>C</u>-(CH₃)₂) and $\delta = 63.58$ ppm (<u>C</u>H-CH₂-S-CH₂) which confirms the introduction of the pendant alkyl sulfonate to the polyimide backbone.

The FTIR spectrum (**Figure 62**) of the sulfonated polyimide derivative **SPI-2** shows the following characteristic absorption bands: (a) at 1779 and 1720 cm⁻¹, due to the asymmetrical and symmetrical C=O stretching vibrations of the imide rings; (b) at 1024 cm⁻¹, assigned to the S=O stretching vibrations of the pendant sulfonate group; and (c) at 730 cm⁻¹, due to the C-N adsorption bands.

The thermal stability of the sulfonated polyimide derivative **SPI-2** was determined by TGA measurements. The TGA thermogram (**Figure 63**) of the sulfonated polyimide derivative **SPI-2** shows a three phase decomposition pattern: (a) a weight loss of 2.8 % between 90 - 150 °C, attributed to the loss of moisture and residual solvent from the polymer; (b) a small weight loss of 1.4 % at 200 – 250 °C, due to the decomposition of the alkyl sulfonate groups; and (c) a weight loss of 34 % at 450 – 600 °C, corresponding to the decomposition of the polymer chain. The TGA data shows that the sulfonated polyimide derivative **SPI-2** is thermally less stable than the polyimide precursor **PI-2**.

The thermal characteristics of the sulfonated polyimide derivative **SPI-2** were determined by DSC analyses. The DSC thermogram (**Figure 64**) of the sulfonated polyimide derivative **SPI-2** shows an onset of molecular motion at 244 °C and a glass transition temperature of 249 °C was recorded. The T_g for the sulfonated polyimide derivative **SPI-2** is higher than the Tg of the polyimide precursor **PI-2** ($T_g = 228$ °C), due to the introduction of the pendant alkyl sulfonate group which increases polymer chain stiffness and consequently a higher T_g value is observed.

The membrane characteristics of the sulfonated polyimide derivative **SPI-2** were determined by atom force microscopy. The AFM image (**Figure 65**) of the dense membrane of the sulfonated polyimide derivative **SPI-2** shows membrane formation with well-defined porosity and low surface roughness. The dark regions in the AFM image of the sulfonated polyimide **SPI-2** represents pores of different sizes and shapes in the range of 52.13 – 299 nm. The light spherical regions are due to the presence of polymer aggregates within the polymer membrane. The AFM image of the sulfonated polyimide derivative **SPI-2** indicates that the membrane morphology has changed with the incorporation of the alkyl sulfonate unit along the polymer chain. The surface roughness value of 7.33 nm was recorded for the sulfonated polyimide derivative **SPI-2** compared to the surface roughness value of 7.96 nm of the polyimide derivative **PI-2**.

The morphology of the sulfonated polyimide **SPI-2** was determined by transmission electron microscopy. The TEM image (**Figure 66**) of the powder form of the sulfonated polyimide **SPI-2** shows spherical multilayer polymer sheets. The cross-section TEM micrograph of the

dense membrane form of the sulfonated polyimide **SPI-2** shows a compacted membrane structure with even porosity throughout the membrane.

The crystallinity of the sulfonated polyimide derivative **SPI-2** was evaluated by X–ray diffraction measurements. The X-ray diffraction pattern (**Figure 67**) exhibits the characteristic amorphous peak between $2\theta = 20^{\circ}$ to 25° .¹⁶¹⁻¹⁶³ The amorphous nature of sulfonated polyimide derivative **SPI-2** may be attributed to (a) the presence of flexible ether linkages, which lower the energy of internal rotation of the polymer chain; and (b) alkyl sulfonate groups pendant to the polymer chain, which reduce the rate of crystallization and the extent of crystallinity.

Elemental analysis of the sulfoanted polyimide derivative **SPI-2** was determined by elemental analysis and gave the following data:

Elemental analysis (calculated): C, 68.01; H, 4.17; N, 4.07; Na, 1.67; O, 17.42. Elemental analysis (found) : C 85.14; H, 5.34; S, 0.53.

The sulphur content of the sulfonated polyimide derivative **SPI-2** was determined by elemental analysis and a value of 0.53 weight percent of sulphur in the polymer was obtained. The ion exchange capacity of the sulfonated polyimide derivative **SPI-2** was calculated using the percentage of sulphur obtained from elemental analysis method according the following equation: ^{134, 135}

IEC = 1000 Sc/ MWs

Where Sc : sulphur content determined by elemental analysis, 0.53 %.

MWs : the molecular weight of sulphur, 32.1 g.

IEC : in mmol/g.

An IEC value of 0.16 mmol/g for sulfonated polyimide **SPI-2** was obtained which compares favourably with the IEC value of 0.91 mmol/g for Nafion-117 with a higher degree of sulfonation.¹⁶⁴

The current research outlines the preparation of a new sulfonated polyimide derivative SPI-2 with the alkyl sulfonate group regiospecifically introduced pendant to the polymer chain. The post-polymerization sulfonation reaction involves the reaction of 1,1-diphenylethylene based polyimide derivative **PI-2** with sodium 3-mercapto-1-propane sulfonate via the classic thiolene polymer functionalization method. The structure of the sulfonated polyimide derivative SPI-2 was determined by dilute solution viscometry analysis, ¹H NMR and ¹³C NMR spectrometry and FTIR analysis. The sulfonated polyimide derivative **SPI-2** is thermally less stable than the polyimide **PI-2** precursor, but a higher T_g value for sulfonated polyimide derivative **SPI-2** is obtained, due to the introduction of the pendant alkyl sulfonate groups which reduces chain flexibility and increase interactions between the sulfonate groups within the polymer chains. The predominantly amorphous character accounts for the excellent membrane properties of the sulfonated polyimide derivative **SPI-2** as evidenced by AFM and TEM analyses. The ion exchange capacity of the sulfonated polyimide derivative SPI-2 with low degree of sulfonation compares favourably to the highly sulfonated commercially available Nafion-117 sample.

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CHAPTER 5

SUMMARY

A novel series of aromatic poly(ether ether sulfone)s, poly(ether ether ketone)s and polyimides based on functionalized 1,1-diphenylethylene derivatives were prepared by step-growth polymerization methods.

The preparation of poly(ether ether sulfone), with the regiospecific introduction of the 1,1diphenylethylene unit along the polymer backbone, was effected by two different synthesis methods. The first method involves the following synthesis steps:

- (a) The synthesis of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane and 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene from bisphenol A and 4,4´-bis(*t*-butyldimethylsiloxy)benzophenone, respectively;
- (b) The cesium catalyzed polymerization reactions of 4,4'-difluorodiphenylsulfone (1) with different mole percentage ratios of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (2) and 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3) in NMP at 150 °C for 12 hours afforded a series of new poly(ether ether sulfone) derivatives with well-defined polymer properties.

The second method involves the following synthesis procedure:

- (a) The novel synthesis of 1,1-bis(4-hydroxyphenyl)ethylene (5) in high yield using 1,1-bis(4-*t*-butyldimethylsiloxyphenyl)ethylene (3) as precursor;
- (b) The potassium carbonate catalyzed polymerization reactions of 4,4'difluorodiphenylsulfone (1) with different mole percentage ratios of bisphenol A (4) and 1,1-bis(4-hydroxyphenyl)ethylene (5) in dimethylacetamide at 165 °C gave a series of new well-defined poly(ether ether sulfone) derivatives.

The preparation of a series of new poly(ether ether ketone) derivatives, with the 1,1diphenylethylene unit introduced regiospecifically along the polymer backbone, was effected by the following synthesis method:

- (a) The synthesis of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane and 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene from bisphenol A and 4,4´-bis(*t*-butyldimethylsiloxy)benzophenone, respectively.
- (b) The cesium fluoride catalyzed polymerization reactions of 4,4′-difluorobenzophenone (6) with different mole percentage ratios of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane
 (2) and 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3) in NMP at 150 °C for 12 hours.

Well-defined poly(ether ether ketone) derivatives with controlled polymer properties and excellent membrane characteristics were obtained.

A series of new polyimide derivatives was prepared via the following synthesis method:

- (a) The synthesis of 1,1-bis(4-aminophenyl)ethylene (9) from 4,4⁻-diaminobenzophenone as the starting material.
- (b) The step-growth polymerization of 4,4'-oxydiphthalic anhydride (7) with different mole percentage ratios of 2,2-bis[4-(4-aminophenoxy)phenyl]propane (8) and 1,1-bis(4-aminophenyl)ethylene (9) in dimethylacetamide via a thermal imidization process afforded well-defined polyimide derivatives with the regiospecific introduction of the 1,1-diphenylethylene unit along the polymer backbone.

Due to the regiospecific introduction of the 1,1-diphenylethylene unit along the polymer backbones of the poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives, a new post-polymerization sulfonation reaction was developed to produce well-defined sulfonated poly(ether ether sulfone), poly(ether ether ketone) and polyimide derivatives whereby the alkyl sulfonate group was regiospecifically introduced pendant to the polymer backbone.

The organic compounds and different polymer derivatives were characterized by size exclusion chromatography and dilute solution viscometry analysis, ¹H NMR and ¹³C NMR spectrometry, FTIR spectroscopy, thermogravimetric analysis and differential scanning calorimetry, thin layer and column chromatography, melting point determination, X-ray diffraction measurements, atomic force microscopy, transmission electron microscopy, elemental analysis, energy dispersive spectroscopy and ion exchange capacity measurements.

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APPENDIX



Figure 1: ¹H NMR spectrum of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (2)



Figure 2: ¹³C NMR spectrum of 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (2)



Figure 3:FTIR spectrum of 2,2-bis(4-t-butyldimethylsiloxyphenyl)propane (2)



Figure 4: ¹H NMR spectrum of 4,4′-bis(*t*-butyldimethylsiloxy)benzophenone



Figure 5: ¹³C NMR spectrum of 4,4'-bis(*t*-butyldimethylsiloxy)benzophenone



 Figure 6:
 FTIR spectrum of 4,4'-bis(t-butyldimethylsiloxy)benzophenone


Figure 7: ¹H NMR spectrum of 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3)



Figure 8: ¹³C NMR spectrum of 1,1-bis[4-(*t*-butyldimethylsiloxy)phenyl]ethylene (3)



Figure 9:FTIR spectrum of 1,1-bis[4-(t-butyldimethylsiloxy)phenyl]ethylene (3)



Figure 10: ¹H NMR spectrum of 1,1-bis(4-hydroxyphenyl)ethylene (5)



Figure 11: ¹³C NMR spectrum of 1,1-bis(4-hydroxyphenyl)ethylene (5)



Figure 12:FTIR spectrum of 1,1-bis(4-hydroxyphenyl)ethylene (5)



Figure 13:Size exclusion chromatogram of the poly(ether ether sulfone) derivative PSU-2



Figure 14: ¹H NMR spectrum of the poly(ether ether sulfone) derivative PSU-2



Figure 15: ¹³C NMR spectrum of the poly(ether ether sulfone) derivative PSU-2



Figure 16:FTIR spectrum of the poly(ether ether sulfone) derivative PSU-2



Figure 17: TGA thermogram of the poly(ether ether sulfone) derivatives PSU-1, PSU-2 and PSU-5



Figure 18: DSC thermogram of the poly(ether ether sulfone) derivative PSU-2



Figure 19:AFM image of the poly(ether ether sulfone) derivative PSU-2



Figure 20:TEM micrograph of the poly(ether ether sulfone) derivative PSU-2



Figure 21: X-ray diffraction pattern of the poly(ether ether sulfone) derivative PSU-2



Figure 22:Size exclusion chromatogram of the sulfonated poly(ether ether sulfone) derivative SPSU-2



Figure 23: ¹H NMR spectrum of the sulfonated poly(ether ether sulfone) derivative SPSU-2



Figure 24: ¹³C NMR spectrum of the sulfonated poly(ether ether sulfone) derivative SPSU-2



Figure 25:FTIR spectrum of the sulfonated poly(ether ether sulfone) derivative SPSU-2



Figure 26: TGA thermogram of the sulfonated poly(ether ether sulfone) derivatives PSU-2 and SPSU-2



Figure 27: DSC thermogram of the sulfonated poly(ether ether sulfone) derivative SPSU-2



Figure 28:AFM image of the sulfonated poly(ether ether sulfone) derivative SPSU-2



Figure 29:TEM image of the sulfonated poly(ether ether sulfone) derivative SPSU-2



Figure 30:X-ray diffraction pattern of the sulfonated poly(ether ether sulfone) derivative SPSU-2



Figure 31Size exclusion chromatogram of the poly(ether ether ketone) derivative PEEK-2



Figure 32: ¹H NMR spectrum of the poly(ether ether ketone) derivative PEEK-2



Figure 33: ¹³C NMR spectrum of the poly(ether ether ketone) derivative PEEK-2



Figure 34:FTIR spectrum of the poly(ether ether ketone) derivative PEEK-2



Figure 35: TGA thermogram of the poly(ether ether ketone) derivatives PEEK-1, PEEK-2 and PEEK-5



Figure 36:DSC thermogram of the poly(ether ether ketone) derivative PEEK-2



Figure 37:AFM image of the poly(ether ether ketone) derivative PEEK-2







Figure 39: X-ray diffraction pattern of the poly(ether ether ketone) derivative PEEK-2







Figure 41: ¹H NMR spectrum of the sulfonated poly(ether ether ketone) derivative SPEEK-2



Figure 42: ¹³C NMR spectrum of the sulfonated poly(ether ether ketone) derivative SPEEK-2


Figure 43:FTIR spectrum of the sulfonated poly(ether ether ketone) derivative SPEEK-2



Figure 44: TGA thermogram of the sulfonated poly(ether ether ketone) derivatives PEEK-2 and SPEEK-2



Figure 45: DSC thermogram of the sulfonated poly(ether ether ketone) derivative SPEEK-2



Figure 46:AFM image of the sulfonated poly(ether ether ketone) derivative SPEEK-2



Figure 47:TEM image of the sulfonated poly(ether ether ketone) derivative SPEEK-2



Figure 48: XRD pattern of the sulfonated poly(ether ether ketone) derivative SPEEK-2



Figure 49: ¹H NMR spectrum of 1,1-bis(4-aminophenyl)ethylene (9)



Figure 50: ¹³C NMR spectrum of 1,1-bis(4-aminophenyl)ethylene (9)



 Figure 51:
 FTIR spectrum of 1,1-bis(4-aminophenyl)ethylene (9)



Figure 52:¹H NMR spectrum of the polyimide derivative PI-2



Figure 53: ¹³C NMR spectrum of the polyimide derivative PI-2



Figure 54:FTIR spectrum of the polyimide derivative PI-2



Figure 55: TGA thermogram of the polyimide derivatives PI-1, PI-2 and PI-5



Figure 56:DSC thermogram of the polyimide derivative PI-2



Figure 57: AFM image of the polyimide derivative PI-2



In powder form

Cross-section of the membrane

Figure 58:TEM micrographs of the polyimide derivative PI-2



Figure 59: X–ray diffraction pattern of the polyimide derivative PI-2



Figure 60: ¹H NMR spectrum of the sulfonated polyimide derivative SPI-2



Figure 61: ¹³C NMR spectrum of the sulfonated polyimide derivative SPI-2



Figure 62:FTIR spectrum of the sulfonated polyimide derivative SPI-2



Figure 63: TGA thermogram of the sulfonated polyimide derivatives PI-2 and SPI-2



Figure 64: DSC thermogram of the sulfonated polyimide derivative SPI-2







In the powder form

Cross-section of the membrane

 Figure 66:
 TEM micrographs of the sulfonated polyimide derivative SPI-2



Figure 67:X-ray diffraction pattern of the sulfonated polyimide derivative SPI-2